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# CHEMICAL CRYSTALLOGRAPHY



AN INTRODUCTION TO  
CHEMICAL CRYSTALLOGRAPHY

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*AUTHORISED TRANSLATION*

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## PREFACE

IN this short treatise on general chemical crystallography the attempt has been made to present the hitherto recognised relations between the properties of crystallised substances and their chemical constitution on the basis of a definite view regarding the structure of crystals. In doing so, a knowledge of the crystallographical laws is assumed, to an extent corresponding to the elementary treatment of them as contained in my text book, *Physikalische Krystallographie*, now appearing in its fourth edition; for information regarding the terms here employed, and also for a fuller introduction to the theory of crystal structure, together with the geometrical ideas requisite thereto, the reader is referred to the above work. In order to secure a maximum of conciseness and brevity in the treatment, it has been necessary to forego entering more fully into the different views which at various times have been propounded regarding the matter in question. Anyone who wishes information regarding the history of the development of chemical crystallography, will find a short historical treatment of the subject in Section III. of the *Introduction to Chemical Crystallography*, by A. Fock (Leipzig, 1888), and especially in the extended English version of the same work, by W. J. Pope (Oxford, 1895); there is a detailed and complete statement in the excellent work by A. Arzruni, *Physikalische Chemie der Krystalle* (Brunswick, 1893), which also constitutes Part I. of Graham-Otto's *Ausführliches Lehrbuch der Chemie*. Subsequent investigations in this field are contained in the various volumes of the *Zeitschrift*

*für Krystallographie*, partly in the form of original contributions, partly as abstracts.

The investigation of the dependence of the properties of crystallised substances on their chemical nature naturally belongs to the domain of physical chemistry, whose votaries, however, during the period of the rapid development of this branch of science, have busied themselves chiefly with the study of amorphous substances (and especially of solutions). Only quite recently have they begun to turn their attention to crystallised substances, and numerous investigations have been published, particularly concerning so-called "mixed crystals," but mostly confined to theoretical deductions from the phase rule, or to the determination and discussion of fusion curves. However valuable such investigations may be, they can never take the place of the exact examination of the crystallisation products themselves (as is evident from the fact that substances have been designated as "isomorphous" merely on the evidence of the fusion curves of their mixtures, even although nothing was known regarding their crystallographical relationships). This arises from the circumstance that the laws observed with amorphous substances cannot be directly applied to crystallised substances, which are essentially so different from them; and especially from the fact that many things of totally distinct nature, whose differentiation still requires further investigation, are thrown together under the name of "solid solutions." The physical crystallographical methods necessary for this have in recent times been so perfected that, in order to shed light on these matters, only their general employment on the part of physical chemists is necessary; and it is an additional aim of this book to discuss the vantage points whence, as the result of further investigation, there might open up the prospect of substituting for the mere isolated relationships which, so far, have been observed to exist between the crystal properties and the chemical constitution of substances, the recognition of some



general law—a goal whose attainment will certainly be made distinctly easier by the great advances which the theoretical investigation of crystal structure has made in recent times. Bearing these points in mind, chemical crystallography should constitute one of the most highly favoured and profitable fields of research in the whole domain of physical chemistry.

In conclusion, it may be remarked that the present work at the same time forms a forerunner to a systematic and critical digest of the now-existing researches on the crystal forms and other physical properties of crystallised substances, which for a series of years I have been preparing. For this work the Royal Academies of Sciences in Vienna, Berlin, Leipzig, and Munich have in recent years placed at my disposal assistance in the persons of Dr Gossner and Dr Hlawatsch; to these must also be added Dr Steinmetz, whose research, frequently mentioned in this work, will shortly be published. As a result of this assistance, it has been possible so to advance the preparations that the printing of the work will soon be commenced.

P. GROTH.

MUNICH, *September* 1904.





## TRANSLATOR'S NOTE

THIS translation of Groth's *Einleitung in die chemische Krystallographie* has been prepared with the co-operation of the author, who has made several alterations rendered necessary by investigations which have been published in the interval between the appearance of the original and the completion of the translation ; he has also kindly read the proof-sheets.

The translator's endeavour has been to adhere as closely as possible to the original in all respects ; consequently, as the latter is intentionally a very condensed statement of the subject, this character may appear even more markedly in the translation.

In order to render the book more readily useful to English-speaking students, additional references have been given, when possible, to abstracts (or, in some cases, to original papers) appearing in the *Journal of the Chemical Society*. Considerable assistance in providing these references, and in reading proofs, has been kindly rendered by Mr A. T. Cameron, M.A.

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## CRYSTAL STRUCTURE AND ITS POSSIBLE VARIETIES

THE molecular hypothesis of matter assumes that in solid bodies the movements of the molecules are limited about certain positions of equilibrium, which are permanently vacated only under the influence of external forces. In a crystallised substance the positions of equilibrium must be characterised by a *regular* arrangement in space, and this arrangement is called the **crystal structure** of the substance.

Physical crystallography, on the one hand, teaches us that the sum total of the regularities which affect the shape and the other physical properties of crystals can be deduced only by means of a general and complete theory of crystal structure ; and, on the other hand, it shows how, from a knowledge of these properties, conclusions may be drawn with regard to the crystal structure of a substance. This necessitates not only a knowledge of the optical properties, the cohesion relationships, etc., of the particular substance, but also, and more especially, a very thorough knowledge of the complete assemblage of crystal faces pertaining to it (crystallising it under as widely different conditions as possible), so as to be able to determine which of the possible faces of the assemblage are the most favoured, under all conditions, with regard to development, *i.e.*, which of them

coincide with the principal planes of the regular structure. If these faces are adopted as the fundamental planes for the proper orientation of the crystal, then the ratios of its primitive parameters are at the same time proportional to the relative distances of the positions of equilibrium along the principal directions in the crystal. There is thus obtained a representation of the internal structure of the crystallised substance, which allows of the known properties of the substance being deduced from this structure; and although we are still in ignorance as to the nature of the internal forces<sup>1</sup> acting on the molecules, we are justified, nevertheless, in assuming that the arrangement thus found represents that of the positions of equilibrium with regard to these forces.

Since the equilibrium in a crystal structure is dependent on the state of motion of the material particles, the stability of this equilibrium must necessarily vary with the temperature. Since, further, every structure may possess several positions of equilibrium (but these of different degrees of stability), it follows that it is only within a certain range of temperature (constancy of pressure being assumed) that any one particular crystal structure represents the most stable amongst the kinds of equilibrium which are possible; outside this range other kinds of arrangement possess more stable equilibrium. If the boundary between two such neighbouring ranges of temperature is transgressed, then the crystal structure hitherto possessed by the substance may indeed continue to correspond to a state of stable equilibrium, but this no longer possesses the highest degree of stability possible. Consequently, under certain circumstances, there takes place a transformation into what is now the more stable condition, and there results a different **modification** of the substance, with different crystal structure and correspondingly different physical properties

<sup>1</sup> Lord Kelvin (*Phil. Mag.* 1902, 4, 139 *et seq.*) has attempted to deduce theoretically, from certain simple assumptions, the possibility of various arrangements with stable equilibrium.



—there has taken place a discontinuous change of the vectorial properties and also, in general, of the scalar properties of the substance.<sup>1</sup>

This property of substances, to assume different crystal structures (and, consequently, different crystalline forms) under different conditions, is called **polymorphism** or **physical isomerism**, and the different states of a substance are said to be **polymorphous modifications** of that substance. Since these states differ only in crystal structure (with all that that implies), the differences disappear as soon as the substance is changed into the amorphous state—whether by fusion, dissolution, or vaporisation. Should, thereafter, differences still persist, then they must be due to differences of structure within the molecules from which the crystals were formed, so that the case is then one of **chemically isomeric** substances. The crystal structures of two chemically isomeric substances are different, just as those of two polymorphous modifications of one substance are.

In both cases, however, there may exist certain similarities between the crystalline forms, and since the general laws regulating the relations between the crystalline forms of polymorphous substances and of isomeric substances have not yet been clearly made out, it is not possible, from any mere difference in the crystal structure of two substances possessing the same chemical composition, to decide whether these are physically or chemically isomeric.

If, however, the two substances react differently after they are fused, dissolved, or vaporised, the discrimination between the two cases becomes indubitable, for then the substances must be chemically isomeric, or polymeric. There are, however, chemically isomeric substances which so readily undergo transformation, the one into the other, that they yield identical products when they are fused, dissolved, or vaporised; and in such a case it is also possible that the crystals of the one isomer may grow in the

<sup>1</sup> A change of pressure, as of temperature, likewise affects the equilibrium conditions, and in accordance with this fact, Tammann has succeeded in proving the occurrence of transformations into modifications which were previously unknown, as, for example, in the case of ice and of phenol.

liquid, solution, or vapour obtained from the other, just as the crystals of one polymorphous modification may grow in the liquid, solution, or vapour obtained from some other modification of the same substance.

A characteristic of polymorphous modifications of one substance is their transformability, the one into the other, without having undergone fusion or evaporation, and without the intervention of a solvent, but merely on change of temperature. This direct transformation from one state of crystallisation into another can be recognised with the greatest certainty by means of O. Lehmann's "crystallisation microscope," which makes it possible to study the behaviour of a preparation while it is being subjected to changing temperatures.<sup>1</sup> Since two polymorphous modifications differ from one another as regards the forms in which they grow, their optical properties, etc., the formation of a new modification during a change of temperature can be at once detected (very easily so with crossed nicols, should one of the two modifications be singly refracting); at the same time it is possible to determine which of the modifications is the stable one at any given temperature, since it grows at the expense of the other. In this way O. Lehmann has proved the existence of various polymorphous modifications for a large number of substances.<sup>2</sup>

The crystallisation microscope can also be used with advantage for the solution of the question whether the isomerism between two substances is chemical or physical. For this purpose one of the two is fused on an object glass, and during the cooling of the fused mass small crystals of the respective substances are brought into contact with it at two different points. Should both crystals grow into the fused mass until they meet, and thereafter one of these crystallisations continue to grow at the expense of the other (renewed heating being requisite in some cases), then the crystals under investigation are two polymorphous modifications of the same substance. Should, however, only one of the crystals employed for "inoculation" grow into the fused mass when brought in contact with it, or, in the event of both growing, should

<sup>1</sup> Concerning this instrument, see O. Lehmann's *Molekularphysik*, Leipzig, 1888, I, 133 *et seq.*; also his *Krystallanalyse*, Leipzig, 1891; further, Groth's *Physikalische Krystallographie*, 3rd edition, 1895, 753 *et seq.*; 4th edition, 1905, 786.

<sup>2</sup> See his *Molekularphysik*, and numerous contributions to the *Zeits. f. Kryst.*, etc.



the two resulting crystallisations remain indifferently side by side when they meet (even after the temperature is raised), then the two substances must be considered as chemically isomeric. The alteration of the temperature is necessary owing to the fact that the rate of transformation of polymorphous substances may be very small at low temperatures, so that in many cases both forms can exist in contact with one another even for years at the ordinary temperature. Further, the possible presence of traces of solvent must be most carefully guarded against, for in the case of certain chemically isomeric (**tautomeric**) substances which transform into one another only in solution, the transformation may be induced by a trace of the solvent, and so the one crystallised state will apparently be transformed directly into the other.<sup>1</sup> At the same time it must be remarked in this connection that, in the case of a number of chemically isomeric substances, observations have been recorded which go to show that even in the absence of every trace of solvent, transformation of the one isomer into the other can take place.<sup>2</sup> On the other hand, transformation through the agency of a solvent can occur also with polymorphous modifications. In doubtful cases, however, it is possible to arrive at a decision as to whether isomerism or polymorphism is present, from a comparison of the melting points of the two crystallised forms.<sup>3</sup>

There is, in addition to chemical isomerism, another phenomenon which must be distinguished from polymorphism, and which we shall call **polysymmetry**. This makes its appearance in substances of so-called **pseudo-symmetric** crystalline form,—that is to say, substances whose crystal structure closely approximates to one of higher symmetry. To this class belong, for example, rhombic, monoclinic or triclinic crystal structures in which the distances between the neighbouring similar material particles, along three directions lying in one plane and intersecting at nearly equal angles, are very slightly

<sup>1</sup> See Schaum, *Annalen aer Chem.* 1898, **300**, 223; also his inaugural dissertation, *Die Arten der Isomerie*, Marburg, 1897.

<sup>2</sup> See Wegscheider, *Sitz. Ber. d. Akad. Wien*, 1901, **110**, ii. 918; *Monats. f. Chem.* **22**, 919; *Journ. C. S.* **82**, ii. 126.

<sup>3</sup> See Wegscheider, *loc. cit.* 919 *et seq.*; 920 *et seq.*; also, more especially, Brunì, *Rend. Accad. Lincei*, Rome, 1902 (5) **11**, i. 386; *Gazz. Chim. Ital.* 1903, **33**, i. 100; *Journ. C. S.* **82**, ii. 448.

different. Such a substance then exhibits a "pseudo-hexagonal" crystalline form, *i.e.*, those faces which together complete an apparently hexagonal form, though not altogether equivalent, are yet, in consequence of the close agreement in the arrangement of the particles in them, so similarly favoured during the formation of the crystal that they regularly appear together and are developed in a similar manner. In this case the crystalline form is apparently hexagonal, and might be imagined as resulting from a really hexagonal crystal by a slight homogeneous deformation, *e.g.*, a rhombic crystal by an extension or compression in the direction of one of the lateral axes, effected uniformly on all parts of the crystal; a monoclinic one by straining in an oblique direction lying in a plane of the hexagonal prism; finally, a triclinic pseudo-hexagonal form by a compression or extension in any general direction. Crystal structures of the kind here described possess, as we learn from physical crystallography, three kinds of positions in which they are in equilibrium with one another, as follows from the fact that they regularly appear as triplet growths, twinned on the faces of the pseudo-hexagonal prism (as so-called **mimetic forms**). In the usual case of these mimetic forms being composed of thin twinned lamellæ, then, the thinner the lamellæ (*i.e.*, the more frequently the three positions alternate with one another in the composition of the whole structure), the more will the variations of the angles from those of a truly hexagonal crystal become obliterated. If, finally, this alternation takes place in a regular manner, and at such minute distances that the twin structure is no longer recognisable even under the microscope, there results a structure which cannot by any of its properties be distinguished from a simple hexagonal crystal. In that case the substance appears in two apparently different modifications, one hexagonal and the other rhombic (or monoclinic, or triclinic) pseudo-hexagonal, with twin structure. Since we have here to do not with a different kind of crystal

structure, as in cases of polymorphism, but with a different mode of composition of the same crystal structure, we shall distinguish as **polysymmetric substances** those which exist in modifications of this kind, possessing different symmetry; the individual modifications, possessing closely agreeing crystalline forms but differing in symmetry, we shall distinguish from the polymorphous as **polysymmetric modifications**.

The re-arrangement into the twinned position, *i.e.*, the formation of twin lamellæ, can be effected by pressure or tension, as also by alteration of the temperature of the crystal. The state of equilibrium for that regular structure in which the crystal appears as quite simple and of higher symmetry, may be a particularly stable one within definite limits of temperature; in such a case, on warming the polysynthetic crystal, not only may the appearance of new lamellæ be observable at first, but as the temperature limit is approached, there may take place gradually an apparent transformation into the more symmetric form. Since this is built up of the same structure as the less symmetric form, but in regular alternation, its properties must be deducible from those of the lower form; with polymorphous modifications such is not the case. As regards the optical properties this deduction is provided by the theory which Mallard developed regarding the optical behaviour of crystalline packets; a peculiarly interesting case of this is exhibited by the enantiomorphous piling up of pseudo-hexagonal lamellæ to form an optically uniaxial crystal exhibiting right or left rotation (quartz).

In the following paragraphs a fuller description is given of a few examples of polysymmetric substances.

**Potassium felspar**,  $\text{KAlSi}_3\text{O}_8$ , is the longest-known example of substances possessing this character. Its crystals sometimes exhibit the properties of quite simple monoclinic individuals; sometimes they are built up of fine lamellæ of a triclinic crystal in two positions, and it is not unusual in such cases to find parts of a crystal which even under the highest magnification exhibit

no recognisable traces of lamellation; these parts, where the behaviour is completely that of a monoclinic crystal, must consequently be looked upon as composed of submicroscopic twin lamellæ.

**Potassium sodium sulphate (glaserite)**,  $K_3Na(SO_4)_2$ , and the analogous **chromate**,  $K_3Na(CrO_4)_2$ , provide additional instructive examples. According to Gossner's investigations they form pseudo-hexagonal (monoclinic) crystals, but always appear in mimetic aggregates which exhibit a nearer approximation to simple crystals of higher symmetry, the higher the temperature at which they were crystallised. Accordingly, they also, on warming, undergo transformation into optically uniaxial structures, without exhibiting any abrupt thermal or volume change.

In the above cases the scalar properties of the two modifications are the same, whilst in the case of polymorphous substances these properties (*e.g.*, density and specific heat) change when transformation takes place. Since, however, the values for these properties are dependent on the pressure, it is possible for the difference between two polymorphous modifications, as regards one of these properties, to become zero at a definite pressure. Such is the case with the two following substances, which at first were supposed to be polysymmetric; later, it was found that under high pressure the transformation is accompanied by change of density, which proves that they belong to the class of *polymorphous* substances.<sup>1</sup>

**Sodium magnesium uranylacetate**,  $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 9H_2O$ , according to Wyruboff's investigations,<sup>2</sup> crystallises at  $15^\circ$  in simple monoclinic crystals which, as regards their angles, differ but slightly from a combination, tabular on the basal plane  $\{111\}$ , consisting of two rhombohedra,  $\{100\}$  and  $\{11\bar{1}\}$ , with a hexagonal bipyramid and the prism of the second kind  $\{10\bar{1}\}$ ; they are therefore pseudo-trigonal. At slightly higher temperatures twin sectors make their appearance, the twinning being on the pseudo-hexagonal prism faces  $\{110\}$  and  $\{130\}$ ; with rising temperature the twin lamellæ become finer and finer, and suddenly the basal table appears singly refracting in parallel

<sup>1</sup> Steinmetz, *Zeits. f. phys. Chem.* 1905, **52**, 449 *et seq.*

<sup>2</sup> *Bull. Soc. Fr. Min.* 1901, **24**, 93 *et seq.*; *Zeits. f. Kryst.* **37**, 191 *et seq.*

polarised light, *i.e.*, the monoclinic crystal has undergone transformation into an optically uniaxial trigonal one. Steinmetz determined the transition temperature to be  $28^\circ$ , and showed by the dilatometric method that the transformation takes place without any change of density; the expansion curve is continuous and almost rectilinear, but with a slight change of direction at  $28^\circ$ , which points to the coefficient of thermal expansion undergoing a slight alteration at that point. There is, however, no measurable thermal effect accompanying the transformation, as shown by the cooling curve obtained by the same observer; under a pressure of 53 atmospheres, however, there is a distinct effect.

**Isopropylammonium chloroplatinate**,  $(C_3H_7NH_3)_2PtCl_6$ , according to Ries,<sup>1</sup> forms apparently rhombic crystals, which, however, are proved by optical investigation to consist entirely of monoclinic lamellæ assembled on the pinacoid {100}. On heating to  $32^\circ$  the lamellæ suddenly disappear, and the crystal shows all the properties of a simple rhombic crystal, which, on cooling below  $32^\circ$ , again becomes transformed into the pseudo-rhombic complex composed of twin lamellæ. With this substance Steinmetz found only a slight decrease of density at the transition point, and the coefficient of expansion appears to be not appreciably different above and below the temperature of  $32^\circ$ ; from the cooling curve there also appears to be no change in the specific heat on transformation.

Amongst pseudo-symmetric or mimetic crystals, however, there are some which do not undergo a transformation into the apparently simple and more symmetric form, but in which a true (*i.e.*, a polymorphous) transformation takes place, as the following examples show:—

**Calcium chloraluminate**,  $Ca_2AlO_3Cl \cdot 5H_2O$ , forms, according to Friedel,<sup>2</sup> apparently hexagonal tables, which, however, are monoclinic triplets; at  $36^\circ$  the boundaries and the slightly re-entrant angles disappear, and the table becomes optically uniaxial. According to Steinmetz's dilatometric determinations, there is a sudden contraction in volume at this point.

**Boracite**,  $Mg_7Cl_2B_{10}O_{30}$  behaves similarly; its pseudo-cubic crystals are built up of numerous rhombic lamellæ, and at  $265^\circ$

<sup>1</sup> *Zeits. f. Kryst.* 1902, **36**, 329.

<sup>2</sup> *Bull. Soc. Fr. Min.* 1897, **20**, 122, *et seq.*; *Zeits. f. Kryst.* **31**, 72; *Journ. C. S.* 1899, **76**, ii, 366.



they are suddenly transformed into singly refracting truly cubic crystals. In this case also there is a distinct contraction, and a considerable absorption of heat.

**Potassium sulphate**,  $K_2SO_4$ , forms rhombic tables which are eminently pseudo-hexagonal, generally with a triplet structure which becomes more pronounced on heating, so that each crystal then appears to be composed entirely of fine lamellæ parallel to  $\{110\}$  and  $\{130\}$ ; simple crystals also give rise to twin lamellæ on heating. Between  $600^\circ$  and  $650^\circ$ , according to Mallard, a sudden transformation takes place into a simple optically uniaxial crystal, whose double refraction is considerably stronger and of opposite sign; this excludes the assumption that it is built up in a regular manner from sub-microscopic lamellæ of the rhombic modification.

**Leucite**,  $KAlSi_2O_6$ , which is pseudo-cubic, behaves in a quite similar manner, and its transformation, at about  $560^\circ$ , into a truly cubic substance is apparently also a polymorphous change. Determinations of the thermal and volume relationships at the transition point have not been carried out on this substance, owing to the high temperature at which the change takes place.

That, finally, one and the same substance can crystallise both in polysymmetric and in polymorphous modifications is indicated by the relationships which are observed in an important mineral group—that of the pyroxenes. The compound  $RSiO_3$ , where R is a bivalent metal (Mg, Mn, Fe, etc.), exists (a) in monoclinic crystals, which often constitute lamellar twin structures of apparently rhombic form; also (b) in rhombic crystals of precisely that form which would result from the above-mentioned twin lamellæ becoming sub-microscopic, and lastly (c) in triclinic crystals of a distinctly divergent form which does not, by twin formation, exhibit gradations towards the two preceding forms. It is therefore to be assumed that the relation between the first and second forms is of the nature of polysymmetry, whilst between these forms and the last one the relation is that of polymorphism, in this case dimorphism.

A further example is supplied by the double sulphates  $KLiSO_4$  and  $NH_4LiSO_4$ . The first of these forms crystals, belonging to the hexagonal pyramidal class, which rotate the plane of polarisation of light, and whose structure may therefore

be looked upon as a spiral polysynthetic one, lamellar on the hexagonal basal plane. The analogous ammonium salt does actually exist in rhombic crystals with eminently pseudo-hexagonal structure ; these frequently form triplets possessing lamellar structure parallel to the basal plane, the lamellæ often being so thin that the crystals appear almost uniaxial and exhibit distinct rotation of the plane of polarisation. This rhombic, or hexagonal, form of ammonium lithium sulphate is not the most stable one at ordinary temperatures, however, and is deposited only from warm solutions ; from cold aqueous solutions a different (polymorphous) modification is produced ; this also forms rhombic crystals, it is true, but has a totally different crystal structure.

Though it appears, from what precedes, that several cases exist in which further investigation is required to show whether the differently crystallised modifications of the substance are polysymmetric or polymorphous, the two phenomena of polysymmetry and polymorphism are so essentially distinct from one another that they must be looked upon as depending on different causes. These differences may be summed up in the following manner :—

*The crystals of that polysymmetric form of a substance, in which the twin growth is no longer recognisable, are only apparently homogeneous bodies, and they differ from the simple or the evidently twinned crystals of the form with lower symmetry only as regards those properties which are conditioned by the way in which they are built up out of the latter. Between the two forms there exist intermediate stages with continuously varying properties, and transformation from the one form into the other does not take place at a definite temperature.*

*Polymorphous modifications, on the other hand, represent really different states (phases). On the transition from one to the other there takes place, in general, a discontinuous change of all the properties, scalar as well as vector, and the transformation takes place at a definite temperature—the transition point (pressure being assumed constant, and leaving out of account retardations due to overheating or overcooling).*

If it is the case, as was assumed in the first instance, that the difference between the polymorphous modifications of a substance depends on a different arrangement of its smallest material particles, the question presently arises: Are these smallest particles, the so-called **crystal molecules**, identical with the chemical molecules, or (as has been widely assumed), are they composed of a number of chemical molecules? Since a direct determination of the molecular weight is possible only for substances in solution or in the gaseous state, attempts have been made to decide this question by employing an indirect method based on the theory of so-called **solid solutions**.<sup>1</sup> The results of these attempts, however, require for their interpretation such manifold assumptions, that this method of determining molecular weights cannot be described as free from objection. It can be shown, however, that the difficulties of the question under consideration are obviated, and the question itself becomes superfluous, as soon as we accept that theory of crystal structure which alone supplies an explanation of all the manifold symmetry observed and possible with crystals, namely, the "Extended Theory of Crystal Structure," propounded by Sohncke in the year 1888.<sup>2</sup> This states that :

*A crystal consists of a finite number of interpenetrating regular point systems, which all possess like and like-directed coincidence movements. Each separate point system is occupied by similar material particles, but these may be different for the different interpenetrating partial systems which form the complex system.*<sup>3</sup>

The points of such a partial system may equally well be supposed to be occupied by similar *atoms*, as by *molecules* (Sohncke, himself, for that matter, had this idea in his

<sup>1</sup> See van't Hoff, *Lectures on Theoretical and Physical Chemistry*, translation by Leffeldt, 2, 70.

<sup>2</sup> *Zeits. f. Kryst.* 14, 431 *et seq.*

<sup>3</sup> That they should be the same is consequently not excluded on this theory, which in itself is purely mathematical ; such a case is improbable, however, on mechanical grounds.



mind (*loc. cit.*), but did not pursue it further); for atoms, like molecules, are possessed of specialised directions, as shown by their valency, by stereo-isomerism and other chemical relations, apart altogether from their possible compound nature and the localised electric charges (or the electric currents circulating about them in a definite manner) in which probably are to be sought the origin of those forces whose equilibrium determines the crystal structure. On that supposition all the atoms in any such partial system would be orientated parallel to one another only in the special case of their forming a simple space lattice; in general the partial system will be formed by the interpenetration of several space lattices which differ in the orientation of the atoms composing them.

If, for example, three regular point systems of this kind, possessing similar coincidence movements and consisting one of sulphur atoms, another of twice as many potassium atoms, and the third of four times as many oxygen atoms, are fitted the one within the other in such a way that equilibrium is maintained, there results a crystal structure with the properties and chemical composition of crystallised potassium sulphate. This structure completely fulfils the condition of "regularity," for within it there exist, at equal but immeasurably small distances, *homologous positions* (those of the similarly orientated atoms of each of the space lattices), *i.e.*, "points, about each of which the mass distribution parallel to any chosen direction in the crystal is the same as about any other."

It is evident, however, that in such a structure "molecules," in the sense in which we speak of gaseous molecules, are altogether wanting, and it is a matter of choice what is to be called the **unit of crystal structure** or the **crystal molecule**; for, just as it is quite arbitrary which mass-points of a regular point system may be supposed to constitute a closer group, so there are various ways in which, with equal right, adjacent potassium, sulphur, and oxygen atoms may be supposed to constitute a  $\text{K}_2\text{SO}_4$

group, or (with twice the number) a  $K_4S_2O_8$  group. The  $K_2SO_4$  molecules exist in the structure only in so far that, when the structure is demolished, by the fusion, dissolution, or vaporisation of the crystal, it is possible for the chemical molecules (or, in some circumstances, multiples of them), to result directly, in consequence of the interpenetration of the regular point systems composed of the different atoms.

It is at once evident that polymorphous modifications must yield identical liquids, solutions, or vapours, if the relative positions of the atoms contained in their structure is similar, and only the point systems (that is to say, the space lattices composing them, which define the crystal structure), and the coincidence operations characteristic of them, are different; for the point systems and space lattices are destroyed on the passage into the amorphous (or the dissolved) state. With chemically isomeric substances, in that volume which contains the neighbouring atoms corresponding to a chemical molecule, the relative position of the atoms is quite different; naturally, in consequence of this, the point systems built up from them are also different, and so is the resultant space lattice characteristic of the whole structure.

In the case of a crystallised element the theory is reduced to that of a single regular point system, composed of similar interpenetrating space lattices in such a way that the atoms form closer groups (Sohncke's "*n*-Punktner"). Since this is possible in various ways, and in addition the space lattices themselves can be different, owing to polymorphism, there is the possibility of a very great multiplicity of modifications in the case of the elements. Those amongst them in which these closer groups of the crystal structure differ as regards number or arrangement of the atoms composing them, break up, on passing into the amorphous or the dissolved state, into molecules which behave as those of chemically isomeric or polymeric substances. This explains the circumstance that certain

"allotropic modifications" of an element may not yield identical solutions or vapours.

Like polymorphism, the relations between crystal form and chemical constitution,<sup>1</sup> to be discussed later, are in accord with the above view as to the structure of crystallised substances, which, as already mentioned, is also capable of explaining all the phenomena of symmetry observed in connection with crystals.

<sup>1</sup> In addition to the relationships designated by the names of morphotropy, isomorphism, etc., which will be treated in subsequent sections, there is one matter which may be referred to at this point. According to the theory here adopted, the crystal structure of those substances whose molecules contain three or six similar atoms, such as:— $\text{Al}_2\text{O}_3$ ;  $\text{NaNO}_3$ ;  $\text{CaCO}_3$ ;  $\text{MgSiF}_6, 6\text{H}_2\text{O}$ ;  $\text{Na}_3\text{Fe}(\text{SO}_4)_3, 3\text{H}_2\text{O}$ ;  $\text{C}_6\text{H}_4(\text{OH})_2$ ;  $\text{C}_6\text{H}_3(\text{COO.C}_2\text{H}_5)_3$ , etc., must contain a point system built up of three-point or six-point groups; now, since the symmetry of this system must exercise an influence on the symmetry of the combined system, the frequent occurrence of trigonal or hexagonal crystal forms with such substances becomes explicable.

## POLYMORPHISM

ACCORDING to the preceding considerations, the idea of polymorphism is to be confined to those homogeneous, physically different states of a substance, in which the difference depends on a difference in their crystal structure. Given that on the transformation of one polymorphous modification into the other there occurs a discontinuous change of properties, the transition point presents certain analogies with the melting point and freezing point. As a matter of fact, there is a thermal effect on changing from a state A, more stable at low temperatures, into a state B, more stable at higher temperatures, and as a rule B possesses a higher specific heat and a lower density than A. At the transition point, A and B are in equilibrium, and this point exhibits the same dependence on pressure which is observed in the case of the melting point, *i.e.*, if the change from A into B is accompanied by an increase of volume, then the transition temperature rises with increasing pressure, in accordance with the same law which applies to the melting point.

Transgression of the transition point, in either direction, may be unaccompanied by transformation, but, like the over-cooling of a liquid below its freezing point, this is possible only if no trace of the new modification is present. If such transgression has taken place, then the substance exists in a state which, as proposed by Ostwald,<sup>1</sup> is designated as **metastable**, because, whilst it corresponds to

<sup>1</sup> *Zeits. f. phys. Chem.* 1897, 22, 302; *Journ. C. S.* 72, ii. 308.

a stable equilibrium, it nevertheless, merely on contact with the other modification which is now the most stable one, is terminated by transformation accompanied by the corresponding thermal effect.<sup>1</sup> On the other hand, that condition in which the transformation commences spontaneously, even without previous contact with the second modification, must be designated as essentially labile. In both cases it is possible for the transformation to take place very rapidly, but it can also be a very slow one, depending on the rigidity of the system. Whilst, in the neighbourhood of the transition point, the tendency towards transformation (and consequently the rate of transformation) naturally increases with the distance from that point of equilibrium, the rigidity of the structure, which resists that tendency, is continually augmented by increased over-cooling, and the result may be that below a certain temperature the rate of transformation is zero; under these circumstances both modifications exist side by side, apparently quite indifferent. Behaviour of this kind has been proved by Gernez in the case of sulphur, and also by Schaum<sup>2</sup> in the case of hexachloroketodihydrobenzene. This explains why aragonite, which is the metastable form of calcium carbonate at ordinary temperatures, can exist unchanged in contact with calcite, the stable form, and changes into the latter only at a somewhat high temperature, in the neighbourhood of the transition point.

We shall now consider in a somewhat more detailed manner several examples of substances whose polymorphous modifications have been investigated, as regards their relations to one another, with some accuracy.

Sulphur can exist in a series of crystallised modifications, two of which—the rhombic one usually obtained by deposition from

<sup>1</sup> From the nature of the difference between polymorphous and poly-symmetric substances it follows that in the latter a metastable condition is not possible.

<sup>2</sup> *Die Arten der Isomerie.*

solution, and the monoclinic one which crystallises from the fused substance—belong to the longest known cases of polymorphism (discovered by Mitscherlich<sup>1</sup>) and have been the most thoroughly studied. The rhombic modification, which possesses the higher density and the lower specific heat is stable up to about  $96^{\circ}$ , when it becomes transformed into the monoclinic form, with absorption of heat (heat is evolved in the reverse process). The transition temperature can be easily exceeded, however, without transformation taking place, and by cautiously raising the temperature (with most careful exclusion of any trace of monoclinic sulphur) it is even possible to bring the now metastable rhombic sulphur into a state of fusion—which takes place at  $113.5^{\circ}$ —without it having undergone transformation into the monoclinic modification; the latter, once it has been formed, melts only at  $119.5^{\circ}$  (according to the observations of Brodie, Gernez, and Muthmann). Conversely, the monoclinic sulphur crystallised from the fused substance, provided all contact with the rhombic form is avoided, can be over-cooled very far, even to the ordinary temperature, without transformation. In that case, however, a spontaneous transformation soon takes place (so that here already we have to deal with a labile condition), and once started it proceeds rapidly. A transgression of the transition temperature never takes place if the other modification is present; it is therefore possible to determine the temperature of equilibrium by examining, with the help of Lehmann's crystallisation microscope (page 4), a preparation in which the two modifications are in contact with each other, and determining the temperature at which no shifting of the boundary between them takes place, to the one side or the other. The determination by means of the dilatometer is more accurate, since on the transformation of rhombic sulphur (density 2.07) into monoclinic (density 1.96), a considerable increase in volume takes place, and on the reverse transformation there is a corresponding contraction. In this way Reicher<sup>2</sup> determined the transition temperature to be  $95.6^{\circ}$ , and showed that it rises with increasing pressure, the increment for one atmosphere being  $0.05^{\circ}$ .

When molten sulphur in a perfectly clean vessel is very carefully cooled below the temperature of solidification, it is

<sup>1</sup> *Abhandl. d. Akad. Berlin*, 1822. *Gesammelte Schriften von E. Mitscherlich*, Berlin, 1896, 190 *et seq.*

<sup>2</sup> *Zeits. f. Kryst.* 1884, 8, 593 *et seq.*



possible to induce, in the over-cooled liquid, the crystallisation of the one or the other modification at will by contact with a crystal of that modification; under otherwise similar conditions, however, the solidification of the liquid to form rhombic crystals is propagated 25-100 times faster than the monoclinic crystallisation.<sup>1</sup> Even below the transition temperature the latter process can be induced in the over-cooled liquid by inoculation with a monoclinic crystal. The transformation of monoclinic solidified sulphur into the rhombic modification, on contact with the latter, naturally proceeds but slowly in the neighbourhood of the transition point; the rate of transformation at first increases, the lower the temperature at which the experiment is conducted, but it reaches a maximum at about  $50^{\circ}$  and thereafter diminishes again, so that at  $-23^{\circ}$  it is almost zero.<sup>2</sup>

Below the transition point, the solubility of monoclinic sulphur is greater than that of the rhombic modification, and it has been shown that, with chloroform, benzene, and ether, the ratio of the solubilities of the two modifications exhibits that relationship to the heat of transformation which is required by theory.<sup>3</sup>

Spring<sup>4</sup> subjected freshly prepared monoclinic sulphur to a pressure of 5000 atmospheres at  $13^{\circ}$ ; the mass was found to have become distinctly harder, and possessed the density and the melting point of the rhombic modification.

Mercuric iodide,  $\text{HgI}_2$ , represents a second example of dimorphism, which also was first demonstrated by Mitscherlich. From solutions it is obtained in red tetragonal crystals, but from the molten mass, or by sublimation, in yellow rhombic crystals. On cooling, the latter transform, with evolution of heat, into aggregates of the red modification, and these can be reconverted into the yellow modification by careful heating. By Schwarz,<sup>5</sup> to whom we owe a very careful investigation of these substances, the transition point was determined to be  $126.3^{\circ}$ . This can be

<sup>1</sup> Gernez, *Compt. rend.* 1883, 97, 1477; *Zeits. f. Kryst.* 11, 102; *Journ. C. S.* 46, 553.

<sup>2</sup> Gernez, *Ann. d. chim. et phys.* 1886, [6] 7, 233; *Zeits. f. Kryst.* 13, 427.

<sup>3</sup> J. Meyer, *Zeits. f. anorg. Chem.* 1902, 33, 140; *Journ. C. S.* 84, ii. 137.

<sup>4</sup> *Bull. Acad. Belg.* 1880, [2] 49, 351.

<sup>5</sup> W. Schwarz, Prize Essay, University of Göttingen, 1892: "Beiträge zur Kenntniss der umkehrbaren Umwandlungen polymorphen Körper," (*Zeits. f. Kryst.* 25, 613). This work also contains a complete summary of the results of earlier investigations.

easily transgressed, for generally it is only at about  $129^{\circ}$  that a partial transformation begins to be apparent, whilst conversely, when no trace of the red modification is present, yellow crystals can be cooled even as far as the ordinary temperature; but then transformation may be induced by contact with any solid body, as for example by scratching. On the transformation of the red modification into the yellow there is a sudden and considerable expansion (Rodwell); and, in accordance with the accompanying thermal effect, the specific heat of the yellow modification is less than that of the red (Schwarz).

*In vacuo*, mercuric iodide vaporises to a considerable extent even at fairly low temperatures, so that the gaseous substance can be obtained both from the red (below  $126^{\circ}$ ) and from the yellow ( $126^{\circ}$ ) modifications. If a cooler solid body is introduced into this vapour, the crystals which deposit on it are always the yellow modification, provided it possessed a perfectly clean surface; should this have been previously lightly rubbed at one spot with crystals of the red modification, at another with those of the yellow, then red crystals deposit on the former and yellow ones on the latter.<sup>1</sup> From solutions, also, both red and yellow modifications can be obtained, the latter even at ordinary temperatures by rapid separation, *e.g.*, from supersaturated solutions, or on formation by double decomposition.<sup>2</sup> This is in accordance with "Ostwald's rule," to be mentioned later.

**Hexachlorethane**,  $C_2Cl_6$ , forms rhombic crystals at ordinary temperatures, but on warming is transformed into a triclinic, and at a still higher temperature, into a cubic modification.<sup>3</sup> Schwarz (*loc. cit.* 45) determined the two transition temperatures, and found the first to be, on warming,  $45-46^{\circ}$ , on cooling,  $43^{\circ}$ ; the second transformation takes place without any transgression of the transition point, either on warming or on cooling, exactly at  $71.1^{\circ}$ . According to experiments by Steinmetz, both transformations (with rising temperature) are accompanied by considerable expansion, so that the rhombic modification (density 2.091, according to Gossner<sup>4</sup>) is the densest, and the cubic one the least dense.

<sup>1</sup> Gernez, *Compt. rend.* 1899, 128, 1516; *Ann. d. chim. e. a. phys.* 1900, [7] 20, 384 *et seq.*; *Zeits. f. Kryst.* 34, 312, *Journ. C. S.* 76, ii. 597.

<sup>2</sup> Lehmann, *Molekularphysik*, 1, 631; Gernez, *Compt. rend.* 1903, 136, 1322; *Journ. C. S.* 84, ii. 481.

<sup>3</sup> O. Lehmann, *Zeits. f. Kryst.* 1882, 6, 584.  
*Zeits. f. Kryst.* 1903, 38, 151.



**Ammonium nitrate**,  $\text{NH}_4\text{NO}_3$ , according to Lehmann's investigations,<sup>1</sup> between the ordinary temperature and its melting point passes through the limits of stability of no less than four modifications; consequently, it is "tetramorphous." The dry salt melts at  $168^\circ$ , the moist salt somewhat lower, since it dissolves in a very small quantity of water; in both cases it solidifies to optically isotropic crystal skeletons. At  $125.6^\circ$  the mass suddenly becomes doubly refracting, and in the case of a solution optically uniaxial crystals are formed (rhombohedra). If the solution cools still further, then, at  $82.8^\circ$  there are produced, from the growths of the former modification, needle-shaped rhombic crystals, orientated in definite directions with regard to the preceding growths. Finally, at  $32.4^\circ$ , these rhombic crystals become transformed into a fourth modification which is also rhombic; this is the one which is obtained in large crystals from aqueous solutions at ordinary temperatures. If this last modification is heated it becomes successively transformed into the three other modifications at the appropriate temperatures. Bellati and Romanese determined the changes in the densities and in the specific heats at the transition temperatures,<sup>2</sup> and Schwarz<sup>3</sup> gave a more exact determination of the transition temperatures; his values have been inserted above in place of those originally found by Lehmann. Bellati and Romanese found for the mean specific heats

From $0^\circ$ - $32^\circ$ (first rhombic modification)	.	.	.	0.407
" $32^\circ$ - $83^\circ$ (second " " )	.	.	.	0.335
" $83^\circ$ - $124^\circ$ (trigonal " )	.	.	.	0.426

and from their determinations Schwarz calculated the densities and their reciprocal values—the specific volumes—of the three modifications, as follows:—

First rhombic modification at $32^\circ$	$d = 1.6560$	$Sp. Vol. = 0.6039$
Second " " { at $32$	1.6021	0.6241
	{ at $83$	0.6299
Trigonal - " at $83$	1.6093	0.6214

On the transformation of the last of these modifications into

<sup>1</sup> *Zeits. f. Kryst.* 1877, 1, 106; *Molekularphysik*, 1, 155.

<sup>2</sup> *Atti. Ist. Sc. Lett.*, etc., Venice, 1886, [6] 4, 1395; *Zeits. f. Kryst.* 14, 78; *Journ. C. S.* 54, 106.

<sup>3</sup> *Beiträge zur Kenntniss der polymorphen Körper*,

the cubic one there is again a considerable increase in volume. In this case, therefore, the first and third transformations take place with increase of volume, the second with contraction; the temperature at which this second transformation takes place must therefore, like the melting point of ice, fall with increase of pressure, in contrast to the two other transition temperatures, which must follow the common rule.<sup>1</sup> The solubility of the first rhombic modification increases regularly with rising temperature up to the transition point; here there is a diminution in the solubility, followed again by a steady increase; on the other hand the transformation into the trigonal modification is coincident with a sudden rise in the solubility, which then again increases in a regular manner with rising temperature (Schwarz, *loc. cit.*).

As is evident from the preceding examples, it is chiefly the temperature which determines the formation of polymorphous modifications; consequently, at different temperatures the one or the other form may be obtained even from the same solution. Nevertheless, the case of mercuric iodide shows that other circumstances as well exercise an influence in determining the production of the one or the other modification. Thus, the salt in whose case Mitscherlich for the first time (1821) demonstrated the phenomenon of dimorphism, namely, sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , crystallises, on cooling a warm aqueous solution, in the usual rhombic form, whilst at lower temperatures and under certain circumstances (not exactly known) a second and very unstable rhombic form is obtained. A case which in this respect has been subjected to much closer investigation, especially through the thorough researches of Vater,<sup>2</sup> is that of the separation of calcium carbonate from carbonic acid solution. Accord-

<sup>1</sup> Tammann, *Krystallisieren und Schmelzen*, Leipzig, 1903, 300.

<sup>2</sup> H. Vater, "Ueber den Einfluss der Lösungs-genossen auf die Krystallisation des Calciumcarbonates," *Zeits. f. Kryst.* 1893, 21, 433-490; 1894, 22, 209-228; 1895, 24, 366-404; 1897, 27, 477-504; 1899, 30, 295-298, 485-508, 31, 538-578; 1901, 35, 149-178,

ing to him it is always the stable<sup>1</sup> trigonal form, calcite, which crystallises out from pure aqueous solutions at temperatures below 30°, whilst from hot solutions, especially on rapid cooling, the metastable rhombic modification, aragonite, separates. But if there are in the solution small quantities of strontium carbonate or lead carbonate, then aragonite may separate even at low temperatures.<sup>2</sup> That even with pure solutions the production of a different modification of a substance may be conditioned by supersaturation, as in the case of mercuric iodide, is further shown by the researches of Lecoq de Boisbaudran<sup>3</sup> on the vitriols; from supersaturated solutions of these salts there separated in the first place, as a rule, that form which at the temperature of the experiment was the less stable. This is always the case when the supersaturated solution is brought into contact with a crystal of the metastable modification, whilst inoculation of it with the stable form of course brings about the crystallisation of the latter. Similarly, the formation of the one modification or the other from the fused mass may be brought about at will by contact with the appropriate crystallised substance, but it goes without saying that it is not possible to bring about the separation of a very slightly stable (labile or metastable) modification if there are present the merest traces of the stable modification. An excellent example of this is supplied by benzophenone,  $\text{CO}(\text{C}_6\text{H}_5)_2$ , which possesses, in addition to the stable rhombic form (m.p. 48-49°) commonly produced, a metastable (probably monoclinic) modification which melts at

<sup>1</sup> That calcite is at ordinary temperatures the stable modification of calcium carbonate, and aragonite the metastable one, is shown by the greater solubility of the latter (Foote, *Zeits. f. phys. Chem.* 1900, **33**, 740; *Zeits. f. Kryst.* **36**, 294; *Journ. C. S.* **78**, ii. 541).

<sup>2</sup> Credner, *Journ. f. prakt. Chem.* 1870 [2] **2**, 292; *Journ. C. S.* **24**, 670.

<sup>3</sup> *Ann. d. chim. e. d. phys.* 1866, [4] **9**, 173; 1869, [4] **18**, 246. See also J. M. Thomson, *Journ. C. S.* 1879, **35**, 196.

26°. This form was first obtained accidentally by Zincke,<sup>1</sup> while preparing the substance, and he found he could reproduce it from the fused material by inoculation with a crystal fragment. Closer investigations into the circumstances under which it is possible to obtain the second modification from the fused mass, instead of the stable one, have been carried out by Schaum<sup>2</sup> and by Schoenbeck.<sup>3</sup>

The spontaneous production of a less stable form of this kind in a molten mass has its analogue in the previously mentioned separation of such a modification from a supersaturated solution (although the less stable form is more soluble, and consequently less removed from its point of saturation, than is the more stable form, which on this ground should first make its appearance); a further analogy is supplied by the phenomena associated with certain chemical reactions. Ostwald<sup>4</sup> has summed up these results in the rule "*that on leaving any state, and passing into a more stable one, that which is selected is not the most stable one under the existing conditions, but the nearest*" (i.e., that which can be reached with the minimum loss of free energy). Ostwald illustrates this rule by means of the curves which represent, for the different states, the dependence of the vapour pressure ( $p$ ), or of the solubility, on the temperature ( $T$ ); somewhere or other these curves must intersect in pairs. Suppose, for example, that *I* (Fig. 1) represents the vapour-pressure curve for rhombic sulphur, *II* that for the monoclinic form, and *S* that for the fused substance; then  $s_1$  and  $s_2$  are the melting points of the two crystallised modifications, and  $u$  is the transition point. "If fused sulphur is over-cooled, we pass along the curve *S* from right to left and arrive, after cutting the

<sup>1</sup> *Ber. d. d. chem. Ges.* 1871, 4, 576; *Journ. C. S.* 24, 832.

<sup>2</sup> *Zeits. f. phys. Chem.* 1898, 25, 722 et seq.; *Journ. C. S.* 74, ii. 369.

<sup>3</sup> *Beiträge zur Kenntniss der polymorphen Körper.*

<sup>4</sup> *Zeits. f. phys. Chem.* 1897, 22, 306; *Journ. C. S.* 72, ii. 308.

curves  $II$  and  $I$  in turn, first in the region of the meta-stable condition and then in that of the labile one. On reaching some point  $x$  in this region, a solid form must appear spontaneously; this, according to the above rule, will not be the form possessing the curve  $I$ , although it is the most stable at this temperature, but the form  $II$  will result, because it is the most adjacent. If  $II$  is then in the metastable region as regards  $I$ , there the matter will rest, and no further transformation will take place unless the product comes in contact with some of form  $I$ . At the same time there is the possibility that  $II$  may be in the labile region as regards  $I$ ; in that case a further spontaneous transformation will set in, and finally the most stable form  $I$  will be reached."

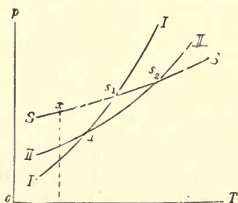


FIG. 1.

Fig. 1 represents the case as it exists with sulphur and many other dimorphous substances. Below the transformation temperature  $u$  the metastable modification  $II$  possesses the greater solubility, and likewise, should it be volatile, the higher vapour pressure,  $p$ ; at the point  $u$  the value of  $p$  is the same for both modifications  $I$  and  $II$ , so that the two are here in equilibrium; beyond  $u$  the modification  $I$ , stable at lower temperatures, becomes the metastable form with higher vapour pressure, while the previously metastable form  $II$  is now the stable one with the lower value for  $p$ , consequently the melting point  $s_1$ , *i.e.* the temperature of equilibrium between modification  $I$  and the fused substance, is lower than  $s_2$ , the melting point of the second modification; thus, for sulphur,  $s_1$  is  $113.5^\circ$ , and  $s_2$  is  $119.5^\circ$  (see page 18).

The case represented in Fig. 2 is also conceivable, however, in which the fusion curve,  $S$ , for the substance lies below the intersection of the curves  $I$  and  $II$ . Under

these circumstances the stable modification *I* will melt at  $s_1$ , without transformation being possible; the metastable form *II*, on the other hand, will melt at a lower temperature

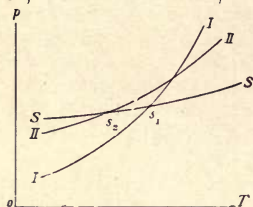


FIG. 2.

$s_2$ , assuming that transformation has not previously been induced by contact with *I*. Substances of this kind will therefore possess two crystallised modifications, one of which is stable at all temperatures below its melting point and never exhibits transformation into the other,

whilst the second modification has a lower melting point and is metastable at all temperatures below that. Benzophenone, mentioned on page 23, is such a substance; for it, consequently, transformation is not a reversible process, as it is for sulphur, etc., but can take place only in one sense, and at any temperature. Lehmann, who, by his researches with the crystallisation microscope (page 4), proved the existence of a considerable number of substances behaving in this way, called those of the first kind **enantiotropic** and those of the second kind **monotropic**; but subsequently he advanced the conjecture<sup>1</sup> that the two are not essentially different, since the transition points and melting points are dependent on the pressure, and therefore it would probably be possible, by applying sufficient pressure to a monotropic substance, to bring the transition point below the melting point, whereby the substance would change into an enantiotropic one.

According to the preceding considerations, which were propounded simultaneously by Ostwald<sup>2</sup> and by Schaum,<sup>3</sup> the difference between the two kinds of polymorphous substances does consist merely in the posi-

<sup>1</sup> *Molekularphysik*, I, 194.

<sup>2</sup> *Zeits. f. phys. Chem.* 1897, 22, 312.

<sup>3</sup> *Arten der Isomerie*, page 24.



tion of the transition point relatively to the fusion curve; and, since increase of pressure shifts the vapour-pressure curves away from the  $T$ -axis, it depends on the difference in the displacements of the various curves whether the transition-point  $u$  and the vapour-pressure curve  $S$  of the fused substance approach one another, or recede, with increasing pressure. There is therefore the possibility of one and the same substance appearing to be monotropic or enantiotropic, according to the pressure.

The displacement of the transition point and the melting point by increasing pressure has been accurately investigated by Tammann<sup>1</sup>; he found that the melting point of monoclinic sulphur and the transition point between it and the rhombic form become steadily higher with increasing pressure, but that the second rises the more rapidly. In consequence of this, the curves representing the dependence of the two temperatures on the pressure meet at a pressure of 1400 kg. and a temperature of  $152^{\circ}$ . At this junction melting point and transition point are identical, and beyond it the transition point would lie above the melting point.

Since the presence of a foreign admixture lowers the melting point of a substance, if the former is soluble in the fused mass, it follows that a displacement of the melting point below the transition point, and consequently the conversion of an enantiotropically dimorphous substance into a monotropic one, can also be effected by means of such an addition. A conversion of this kind was first obtained by Schenck and Schneider<sup>2</sup> in the case of *p*-azoxyanisole, which at  $116.8^{\circ}$  undergoes transformation into a second and "liquid crystalline" modification, which in its turn melts at  $134^{\circ}$ , *i.e.*, it forms then a truly isotropic liquid. By addition of benzophenone this melting point can be lowered as far as  $108.4^{\circ}$ , that is to say  $8.4^{\circ}$  below the transition temperature, so that the substance then behaves as a monotropically dimorphous one. Carbon tetrabromide,  $\text{CBr}_4$ , crystallises after fusion (m.p.  $92.5^{\circ}$ ) in cubic crystals, which at  $46.9^{\circ}$  become transformed into the monoclinic modification which is stable at ordinary temperatures; according to the investigations of Rothmund<sup>3</sup> this transi-

<sup>1</sup> *Krystallisieren und Schmelzen*, 269.

<sup>2</sup> *Zeits. f. phys. Chem.* 1899, **29**, 546; *Journ. C. S.* **76**, ii. 637.

<sup>3</sup> *Zeits. f. phys. Chem.* 1897, **24**, 712; *Journ. C. S.* **74**, ii. 158.

tion point is lowered by the addition of carbon tetrachloride, proportionally to the quantity of the latter, to the extent of  $1.6^{\circ}$  for 2 mol. per cent. Since carbon tetrachloride is liquid, and solidifies, even below  $0^{\circ}$ , only under high pressure, it is probable that the lowering of the melting point of carbon tetrabromide, by addition of the chloride, is much greater than that of the transition point, and a moderate addition of tetrachloride might suffice to convert the enantiotropically dimorphous tetrabromide into a monotropically dimorphous substance.

Just as, in a greatly overcooled liquid, the internal friction in many cases becomes so great that the growth of crystals in it can take place only with extreme slowness, it is likewise found, in the transformation of polymorphous substances from one modification into another, that, though the rate of transformation certainly increases when overcooling below the normal transition point has taken place, it nevertheless reaches a maximum at a certain degree of supercooling; beyond this point the rate diminishes again. Gernez (see page 19) has proved this behaviour in the case of enantiotropic sulphur, and Schaum<sup>1</sup> found that the two modifications of the monotropically dimorphous hexachloro-keto-dihydrobenzene,  $C_6Cl_6O$ , when their formation had been brought about in the one preparation of the substance, could at ordinary temperatures exist unchanged for years in contact with one another; whilst, on gently warming the preparation, the transformation immediately proceeded. In this respect also, therefore, these two kinds of polymorphous substances appear not to be different.

The simultaneous formation of different polymorphous modifications in a solution is a phenomenon which is at least analogous to the above-mentioned indifference towards direct transformation; the following substances exhibit this peculiarity:—

**Telluric acid**,  $H_6TeO_6$ , crystallises both cubic (in octahedra) and monoclinic (in pseudo-trigonal doublets and triplets). From hot nitric acid of a certain concentration both modifications are formed side by side; a gradual transformation of the cubic form

<sup>1</sup> *Die Arten der Isomerie*, 47.

into the monoclinic takes place only with dilution of the nitric acid. In the dry state both forms are very stable, and no transformation of the one into the other takes place.<sup>1</sup>

**Ammonium fluosilicate**,  $(\text{NH}_4)_2\text{SiF}_6$ , crystallises from aqueous solution at temperatures above  $13^\circ$ , cubic, and below  $6^\circ$ , hexagonal; between these two temperatures both modifications are formed side by side, and undergo no alteration at ordinary temperature; the hexagonal form becomes transformed into the cubic only when it is heated along with some of the solution on the water bath. In the dry state both modifications can exist side by side for an indefinite period, provided the temperature is not high; only towards  $100^\circ$  do the hexagonal crystals fall to a powder, which probably consists of the cubic form.<sup>2</sup>

**Di-*m*-nitro-*s*-diphenylcarbamide**,  $\text{CO}(\text{NH}.\text{C}_6\text{H}_4\text{NO}_2)_2$ , exists in three modifications:  $\alpha$ , yellow prismatic crystals;  $\beta$ , white needles;  $\gamma$ , yellow tablets. When a solution of one of these forms, or of a mixture of them, is prepared in boiling alcohol of 95 per cent., and, after having been filtered while warm into a flask kept at constant temperature by immersion in an oil bath, is caused slowly to evaporate by leading through it a current of dry air, then, between  $75^\circ$  and  $30^\circ$ , crystals of the  $\alpha$  and  $\beta$  modifications are always obtained side by side, even when the solution, saturated at the given temperature, has been inoculated with crystals of one kind. At the higher temperatures more crystals of the  $\alpha$  modification are obtained; at the lower ones, more of  $\beta$ . Specially good crystals are obtained at  $60^\circ$ . The inoculation with crystals of one kind merely results in increasing and accelerating the separation of that particular form, with retardation of the formation of the other one; in this way, however, the development of specially good crystals of the second form is favoured. If the filtered mother-liquor is allowed to evaporate by exposure to air at the ordinary temperature ( $13^\circ$ ), then the third modification,  $\gamma$ , alone crystallises out. If the solution is warmed a few degrees, however, then a few crystals of  $\beta$  also appear; at  $40^\circ$ ,  $\gamma$  entirely disappears, and  $\alpha$  appears in small quantities, increasing with rising temperature. Accordingly, so far as separation from alcoholic solution is concerned, the  $\gamma$  modification is the most stable at ordinary temperatures, the form  $\beta$  at  $50$ - $60^\circ$ , and  $\alpha$  at higher temperatures. This behaviour may be modified by the solvent, however; for, from

<sup>1</sup> Gossner; *Zeits. f. Kryst.* 1903, **38**, 501.

<sup>2</sup> Gossner, *loc. cit.* 147.

glacial acetic acid, or from a mixture of it with alcohol, only the white needles of  $\beta$  are obtained on cooling, and such is also the case on preparation in presence of hydrochloric acid. If the  $\gamma$  crystals are heated to  $60^\circ$ , they become opaque and then white; towards  $180^\circ$ , the  $\beta$  crystals become opaque and then yellow; the  $\alpha$  crystals melt at  $242^\circ$  without previous change, and this temperature is also the melting point of the transformation products of the  $\beta$  and  $\gamma$  modifications.<sup>1</sup>

The following can also be obtained side by side from solutions:—The rhombic and the monoclinic modification of **sodium beryllium fluoride** ( $\text{Na}_2\text{BeF}_4$ )<sup>2</sup>; the two forms, entirely different in structure, of **dimethylammonium chloroplatinate** ( $\text{NH}_2(\text{CH}_3)_2\text{PtCl}_6$ , according to le Bel<sup>3</sup>; the monoclinic and the triclinic modification of **rubidium bichromate**,  $\text{Rb}_2\text{Cr}_2\text{O}_7$ ,<sup>4</sup>; the two forms of **ammonium paratungstate**,  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\cdot\text{H}_2\text{O}$ <sup>5</sup>; of **mannitol**,  $\text{C}_6\text{H}_{14}\text{O}_6$ <sup>6</sup>; of **m-diamidobenzenesulphonic acid**,  $\text{C}_6\text{H}_3(\text{NH}_2)_2\text{SO}_3\text{H}$ ,<sup>7</sup> etc.

In these and many other cases, the direct transformation of the one crystallised modification into the other has not been proved—as a rule, no attempt has been made to do so. Since, further, for most of the substances (especially the organic ones) which are known in different crystalline forms, the densities of the two modifications are unknown, it is possible that in some of the cases we have to deal with polysymmetric substances, especially when the two forms correspond to very similar crystal structures. This is the case, for example, with the two modifications of the above-noted examples of ammonium paratungstate and of mannitol; also with the monoclinic compound  $\text{CuNO}_3\text{OH}\cdot\text{Cu}(\text{OH})_2$  (prepared by Wells and Penfield), whose density differs but slightly from that (which probably could be only approximately determined) of the rhombic mineral, **gerhardtite**, which crystallises quite

<sup>1</sup> Offret and Vittenet, *Bull. soc. fr. min.* 1899, **22**, 69; *Zeits. f. Kryst.* 1901, **34**, 627; *Journ. C. S.* **76**, 1, 886.

<sup>2</sup> Marignac, *Arch. sc. phys. nat.* 1873, **46**, 196; *Journ. C. S.* **27**, 24.

<sup>3</sup> See Ries, *Zeits. f. Kryst.* 1902, **36**, 330.

<sup>4</sup> Wyrouboff, *Bull. soc. fr. min.* 1881, **4**, 120; *Zeits. f. Kryst.* **8**, 639.

<sup>5</sup> Marignac, *Ann. Chim. phys.* 1863 [3], **69**, 24.

<sup>6</sup> Zepharovich, *Zeits. f. Kryst.* 1888, **13**, 145.

<sup>7</sup> Levin, *Zeits. f. Kryst.* **7**, 521.

similarly<sup>1</sup>; undoubtedly polysymmetric (trigonal and pseudo-trigonal) is **cerium silicotungstate**,  $\text{Ce}_4(\text{W}_{12}\text{SiO}_{40})_{39}81\text{H}_2\text{O}$ .<sup>2</sup>

It has already been stated on page 16 that, as a rule, that modification of a polymorphous substance which is stable at higher temperatures possesses the lower density, and such, as a matter of fact, is the case for the following among the examples already fully treated, namely—Sulphur (page 17), mercuric iodide (page 19), and hexachlorethane (page 20); and, in addition, for quartz and tridymite, as also for a series of other substances for which the densities of the different modifications are known. On the other hand, there has been already mentioned (page 21) a substance, ammonium nitrate, which shows the opposite character. It is true that the transformation of the first rhombic modification into the second rhombic one follows the above rule, but the transformation of the second rhombic modification into the trigonal one is accompanied by an increase of density. The same is the case with the transformation of trigonal silver iodide,  $\text{AgI}$ , into the cubic form, which is stable at higher temperatures; also with dipropylammonium chloroplatinate,  $(\text{NH}_2(\text{C}_3\text{H}_7)_2)_2\text{PtCl}_6$ , which, according to Ries, forms two monoclinic modifications of totally different crystal structure; further, also, with the transformation of boracite into the cubic form (page 9), and of the monoclinic calcium chloraluminat into the trigonal modification (page 9). Analogous cases, in which the modification corresponding to the higher temperature is likewise the denser, are those of arsenious oxide,  $\text{As}_2\text{O}_3$ ; antimonious oxide,  $\text{Sb}_2\text{O}_3$ ; also calcite and aragonite,  $\text{CaCO}_3$ ; potassium calcium chromate,  $\text{K}_2\text{Ca}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ ; and, among the elements, phosphorus and arsenic (whilst carbon is normal).

Since, amongst the above-mentioned polymorphous substances of the second kind, there are cases, such as those of

<sup>1</sup> *Zeits. f. Kryst.* 1887, **11**, 303.

<sup>2</sup> Wyrouboff, *Bull. soc. fr. min.* 1896, **19**, 219 *et seq.*; *Zeits. f. Kryst.* 29, 667.



silver iodide and boracite, in which the modification which is stable at higher temperatures belongs to the cubic system, or, at least, possesses higher symmetry than the other modification, as in the case of ammonium nitrate and calcium chloraluminat, it might be supposed that the contraction on transformation was caused by the assumption of higher symmetry of crystal structure, with a resultant denser arrangement. This, however, is contradicted by the knowledge that, with phosphorus, arsenic, arsenious oxide, and antimonious oxide, as well as with calcium carbonate, precisely the reverse is the case, since with them the modifications which are stable at lower temperature possess the higher symmetry and the lower density.

Quite similar relations are found with those substances which follow the first-mentioned rule : the form with higher symmetry may possess the higher density, and consequently correspond to the lower temperature, as in the cases of carbon, sulphur, tin (tetragonal and rhombic), and mercuric iodide ; or the form stable at higher temperatures, and possessing the lower density, may exhibit a higher symmetry, as, for example, the cubic modification of telluric acid, of ammonium and potassium fluosilicates, of hexachlorethane, of ammonium nitrate (as compared with the trigonal or hexagonal modification). Similarly, the monoclinic form of carbon tetrabromide becomes transformed at  $46.9^{\circ}$  into a cubic modification, with considerable increase of volume (Steinmetz) ; and various polymorphous chloroplatinates behave similarly, according to the investigations of Ries.

The number of polymorphous substances which become transformed at higher temperatures into a cubic (singly refracting) modification is strikingly large ; but, as the above examples show, this may be accompanied by either an increase or a decrease of volume. The former case is the commoner, evidently because the majority of substances follow the rule that the form corresponding to the higher temperature possesses the lower density. On the other hand there also exist, in both classes of substances, cases where the



modification corresponding to the lower temperature crystallises in the cubic system.

As in the matter of symmetry, so also in the matter of the crystallographic dimensions, is it found that the relations between the different modifications of polymorphous substances are very various. In many there is an evident similarity in the crystal structures of the two modifications.<sup>1</sup>

**Carbon tetrabromide**,  $\text{CBr}_4$  (page 32), crystallises at ordinary temperatures in monoclinic crystals, whose shape differs from that of a regular octahedron (tabular on one pair of faces) only by very small variations in the angles, and which cleave parallel to the predominating pseudo-octahedral face. At  $46.9^\circ$  the crystals become singly refracting, without losing their transparency, and consequently have undergone transformation into truly regular octahedra.

**p-Nitrophenol**,  $\text{C}_6\text{H}_4\text{OHNO}_2$ , crystallises at ordinary temperatures in monoclinic prisms; from warm solutions and from the fused substance a modification which is metastable at ordinary temperatures is obtained, consisting of prisms whose angles are almost identical with the prism angles of the stable modification; the axial inclinations of the two forms likewise differ but little from one another, and the  $c$  parameters stand almost exactly in the ratio 2 : 1, so that the two substances were assumed by earlier investigators to be identical. Naturally, they differ as regards their physical properties, cleavage, optical behaviour, etc.<sup>2</sup>

**Mannitol** (page 30) exists in two rhombic modifications of very similar form, possessing the same cleavage; their mutual relations require further investigation, however.

Finally, attention may be called to Beckenkamp's views regarding the relationships between the crystal structures of **quarz** and **tridymite**.<sup>3</sup>

The number of such examples might be further increased by numerous cases in which conclusions regarding the form of the one modification can be drawn only indirectly from that of some chemically analogous substance; in any case the relations between

<sup>1</sup> The inevitable similarity between those forms which stand to one another in the relation of polysymmetry naturally does not come into consideration here; only that between truly polymorphous modifications.

<sup>2</sup> O. Lehmann, *Zeits. f. Kryst.* 1877, **1**, 45.

<sup>3</sup> *Zeits. f. Kryst.* 1901, **34**, 579 *et seq.*

the cubic and the pseudo-cubic modifications of phosphorus, arsenic, boracite, leucite, etc., fall also to be included here.

On the other hand, the closer investigation of the various modifications of a substance generally shows that, even where certain similarities between the angles occur, there are always profound differences observable—in the cohesion, with respect to the crystal forms specially favoured during the growth of the crystal, and in other properties—which point to an essential difference of crystal structure in the various modifications.

The reason why, as yet, no general rules governing the relations between the crystal structures of the different modifications of a polymorphous substance have been recognised, is to be sought in the fact that, so far, there are only a very small number of substances whose different modifications have been studied so fully, from the crystallographical point of view, that a decision regarding their crystal structure can be arrived at with some degree of probability; the list at present consists almost entirely of isolated examples. An insight into the regularities which doubtless exist would be possible only if there were accurate physico-crystallographical investigations of the various crystalline modifications of different series of substances which exhibit, as regards their chemical constitution, close relations of a well recognised nature. In any such systematic investigation of these questions difficulties would certainly arise in many cases, owing to the circumstance that for two chemically related substances, even when they possess a quite analogous constitution, the limits of temperature and pressure within which their different modifications are stable may differ very greatly from one another. This is generally the case, for example, with the analogous compounds of chlorine, bromine, and iodine. Among these, the compounds of iodine generally possess the highest melting point, other conditions being the same; consequently, for many iodine compounds the transition temperature between two modifications lies above the ordinary temperature, whilst

for the corresponding chlorine and bromine compounds it lies much below the ordinary temperature. As a result, the iodine compound is obtained under ordinary conditions in a form which, when heated, undergoes transformation into a new modification before melting. Those forms of the chlorine and bromine compounds which correspond to the first modification of the iodine compound, would be formed only at a temperature so low that proof of the transformation, and crystallographic examination of the new form, would no longer be possible. Since monotropic modifications melt at different temperatures, it may well be that the anomalies as regards melting point, observable with many organic compounds, are in most cases due to the fact that the anomalous melting point is that of a different modification.

## THE COMPARISON OF THE CRYSTAL STRUCTURES OF CHEMICALLY ALLIED SUBSTANCES (MORPHOTROPY)

THE recognition of the laws governing the dependence of the crystal structure of a substance on its chemical constitution, forms the ultimate goal of chemical crystallographical research. The road thereto can be found only by comparison of the crystal structures of numerous series of chemically allied substances. Since, however, substances in general are capable of assuming different crystal structures under different conditions, the relationships between the structures of two substances can, naturally, be recognised only when the **corresponding states** of the two are compared. For the reasons given at the end of the preceding section, however, these are in many cases unobtainable ; or, at least, the properties of the one substance in that state cannot be determined so completely as to allow of its crystal structure being deduced therefrom with anything like probability. In spite of these difficulties, and the consequent incomplete character of the material available for comparison, it has nevertheless been possible to recognise certain relationships between the crystal forms of substances whose chemical constitution exhibits a definite relationship ; and, as might be expected, the connection is the more intimate, and therefore the more striking, the closer the substances concerned stand to one another as regards chemical character. Hence it arose that the cases in

which the close agreement in crystal structure was first recognised were those of substances whose chemical constitution exhibits complete analogy, *e.g.*, that of two salts formed by the same acid with two closely related metals of like valency, or that of two salts of the same metal with two completely analogous acids, such as ortho-phosphoric and ortho-arsenic acids. This agreement was called **isomorphism** by its discoverer, Mitscherlich; it will receive detailed treatment further on.

In general, the question as to the relation between the crystal structures of two substances, which stand in definite chemical relationship to one another and which are known in corresponding states, will be answered when it can be stated what change the crystal structure of the one substance undergoes when those changes in the chemical molecule, by which it is transformed into the second substance, are imagined to be carried out. This change in the crystal structure can be looked upon as the analogue of a *homogeneous deformation*, since by it a homogeneous system—the crystal structure of the first substance—is converted into a second, likewise homogeneous, system—the crystal structure of the second substance.

According to the theoretical views to which the study of the physical properties of crystals has led, the essence of the crystal structure of a substance is the fundamental space lattice, *i.e.*, the arrangement of homologous points, such as all similar and similarly orientated atoms. But from a knowledge, as complete as may be, of the assemblage of crystal faces of a substance, from its cohesion, twinning, etc., we are enabled to decide as to the most probable form of the space lattice. If, now, we refer the faces of the crystal to the planes of the appropriate primitive parallelepiped, then the so-called crystal elements (*i.e.*, the parametral ratios  $a : b : c$ , and the axial angles  $\alpha, \beta, \gamma$ ) simultaneously give us the relative lengths of the sides of the parallelepiped, and its angles. If now we imagine the space occupied by the structure of the crystal to be divided into space units

such that in each there are contained the atoms corresponding to a chemical molecule, then, naturally, the centres of gravity of these space units form the same space lattice, and, with the proviso made above, the parameters of the crystal determine the relative distances of these centres from one another.

The usual crystallographic axial ratios, however, state these relative dimensions for each substance in such a way that one of them serves as unit, whilst the relation in which this unit stands to that for any other substance remains unknown. From considerations which were advanced simultaneously by Becke and by Muthmann<sup>1</sup> (in the first instance, however, only with a limitation to **isomorphous substances**, *i.e.*, such as stand to one another in the relation of isomorphism, as mentioned on the previous page), there appears to exist a possibility of determining the ratio of these units for different substances which it is desired to compare with one another, or, in other words, of referring to the same unit the relative distances between homologous points in the structures of such substances.

The space units (as defined above) of the crystal structures of two different substances contain each a chemical molecule of the respective substances; their masses must therefore stand in the same ratio to one another as the molecular weights of the two substances. If, now, we assume two crystallised substances to have the same density  $d$ , but different molecular weights,  $M$  and  $M'$  respectively, it is evident that the volumes of the space units of their crystal structures must be in the proportion of the molecular weights; for a given volume of the one substance, which, let us say, possesses a molecular weight twice that of the other, would then consist of only half as many space units

<sup>1</sup> F. Becke, "Ueber Molekulare Axenverhältnisse," *Anzeiger d. K. Akad. d. Wiss. Wien.* 1893, **30**, 204. W. Muthmann, "Beiträge zur Volumtheorie der krystallisierten Körper," *Zeits. f. Kryst.* 1894, **22**, 497. E. H. Kraus and G. Mez, "Über topische Axenverhältnisse," *Zeits. f. Kryst.* 1901, **34**, 389.



as the same volume of the other substance, so that the space units of the latter must be twice as large. If, on the other hand, the molecular weights of two crystallised substances were the same, but their densities,  $d$  and  $d'$ , different—say, the one double the other—then a given volume of the substance with the higher density would contain twice as many space units as the same volume of the other; the space units of the latter would therefore be only half the size of the former, or, stated generally: the volume of the space unit is inversely proportional to the density,  $d$ . If the volumes of the space units of the crystal structures of two substances are designated by  $V$  and  $V'$ , then the relationship between them is expressed by the equation—

$$V : V' = M / d : M' / d'$$

*i.e., The volumes of the space units in the crystal structures of different substances are proportional to the quotients obtained by dividing the molecular weights of the substances by the densities.* These quotients are called the **equivalent volumes** (or **molecular volumes**) of the substances.

If the volume,  $V$ , of the space unit of the crystal structure of each crystallised substance is taken as equal to its equivalent volume, the volumes of these space units are thereby referred to the same unit, namely to the space unit of a crystallised substance with molecular weight equal to its density, for in this case  $V = 1$ . If this space unit had the shape of a cube, the length of an edge would be the appropriate unit of length, and to this unit of length would be referred the parameters of the primitive parallelepipeds of every crystallised substance when these were calculated by the help of the volume  $V$ , as determined from the molecular weight and the density. These values are called the **topic parameters** of the substance, since they follow from the manner in which the substance fills space; they are indicated by the symbols  $\chi$ ,  $\psi$ ,  $\omega$ .

The shape of the units, into which the whole space occupied by the crystal is to be imagined as divided, depends on the nature of the space lattice which forms

the foundation of the structure, and the calculation of the topic parameters varies according to this shape.

1. In the most general case, that of a **triclinic** space lattice, it is evident that the shape of the space unit is identical with that of the elementary parallelepiped of the lattice. For, if we imagine the space occupied to be divided up parallel to the sides of this parallelepiped into equal units of the same shape and size, the centres of gravity of these units reproduce an exactly similar

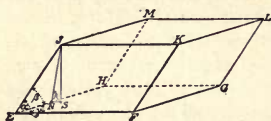


FIG. 3.

space lattice. In any such parallelepiped (Fig. 3) let the sides  $EH = \chi$ ,  $EF = \psi$ , and  $EJ = \omega$ , and further,  $JS$  be the normal to the basal plane  $EFGH$ , and  $SN$  perpendicular to  $EH$  (so that

$A$  is the angle between the planes  $EFGH$  and  $EHMJ$ ), then <sup>1</sup> the volume of the parallelepiped is given by the equation

$$V = \chi\psi\omega \sin \beta \sin \gamma \sin A.$$

If the ratios  $EH : EF : EJ$  are given as usual by the crystallographic axial ratios  $a : b : c$ , so that  $\chi : \psi = a$ , and  $\omega : \psi = c$ , then the following values are obtained for the topic parameters :—

$$\begin{aligned}\psi &= \sqrt[3]{\{V / ac \sin \beta \sin \gamma \sin A\}} \\ \chi &= a\psi = \sqrt[3]{\{a^2V / c \sin \beta \sin \gamma \sin A\}} \\ \omega &= c\psi = \sqrt[3]{\{c^2V / a \sin \beta \sin \gamma \sin A\}}.\end{aligned}$$

2. If the space lattice is **monoclinic**, with the angles  $A, a$ , and  $\gamma = 90^\circ$  (Fig. 4), then the above equations reduce to the following :—

$$\begin{aligned}\chi &= a\psi = \sqrt[3]{\{a^2V / c \sin \beta\}} \\ \psi &= \sqrt[3]{\{V / ac \sin \beta\}} \\ \omega &= c\psi = \sqrt[3]{\{c^2V / a \sin \beta\}}.\end{aligned}$$

3. If the elementary parallelepiped has the form of a rhombic prism with oblique base, the same formulæ give  $\chi$  and  $\psi$  as the diagonals of the base, and from these the sides follow directly, whilst  $\omega$  is the height. As is evident from Fig. 4, the volume of this prism is exactly half of that of the parallelepiped  $EFGHJKLM$ .

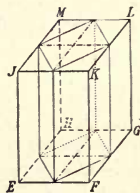


FIG. 4.

<sup>1</sup> Kraus and Mez, *loc. cit.*

4. If the elementary parallelepiped is rectangular (corresponding to the rhombic system), then the lengths of its three sides are :—

$$\begin{aligned}\chi &= a\psi = \sqrt[3]{\{a^2V / c\}} \\ \psi &= \sqrt[3]{\{V / ac\}} \\ \omega &= c\psi = \sqrt[3]{\{c^2V / a\}}.\end{aligned}$$

5. In the case of a rhombic prism with right base, there is the same relation between this parallelepiped and the preceding one, as was shown between cases 3 and 2; it is only necessary to suppose, in Fig. 4, the sides JM, KL, etc., perpendicular to EJ, etc.

6. From the rectangular parallelepiped space lattice another can be derived, in which the centres of the parallelepipeds also are points of the lattice.<sup>1</sup> If we imagine all the points of such a lattice as middle points of the space units, then these no longer have the form of a **triparallelohedron**, consisting of three pairs of parallel planes, which so far has been the only case considered, but of a **heptaparallelohedron** corresponding to a combination of a rhombic bi-pyramid with the three pinacoids (see under 12). The volume of this unit is just half of that of the rectangular parallelepiped, for the number of lattice points in a given space is twice as great as in the rectangular parallelepiped lattice.

7. From the space lattice 5 still another can be similarly derived, in which the lattice points form the corners of rhombic bi-pyramids.<sup>2</sup> If these are imagined as centres of space units, the latter will then have the form of a **hexaparallelohedron**, corresponding to a combination of the three rhombic prisms  $\{110\}$ ,  $\{101\}$ ,  $\{011\}$  (see under 13). The volume of this unit is half of that of the corresponding rhombic prism, since twice as many of them are contained in the same space.

8. In the **tetragonal** prismatic space lattice the elementary parallelepiped is again rectangular, and  $a = b$ ; consequently

$$\begin{aligned}\chi &= \psi = \sqrt[3]{\{V / c\}} \\ \omega &= c\psi = \sqrt[3]{\{c^2V\}}.\end{aligned}$$

<sup>1</sup> *Physikalische Krystallographie*, third edition, fig. 140 d; fourth edition, fig. 156 d.

<sup>2</sup> *Phys. Kryst.*, third edition, fig. 140 b; fourth edition, fig. 156 b.

9. If the centres also of the prisms are lattice points, then twice as many of these are present; the space units (which, consequently, are only half the size) are **hexaparallelohedra**, corresponding to a combination of the tetragonal prism  $\{110\}$  and the bi-pyramid of the second kind  $\{101\}$ .

10. In the **rhombohedral** space lattice, and the triparallelohedral space unit identified with it, we have, for the sides,  $a=b=c$  and, for the angles,  $\alpha=\beta=\gamma$ ; consequently

$$\chi = \psi = \omega = \sqrt[3]{\{V / \sin^2 A \sin A\}},$$

where  $A$  is the supplement of the measured angle between the faces of a polar edge of the rhombohedron, and is given by the equation,

$$\sin (A/2) = \sin (a/2) / \sin a.$$

11. In the **cubic** space lattice,  $a=b=c$  and  $\alpha=\beta=\gamma=90^\circ$ ; consequently

$$\chi = \psi = \omega = \sqrt[3]{V}.$$

As mentioned on page 39, the three topic parameters of such a space unit would assume the value 1 if  $V=1$ , *i.e.*, if the molecular weight were equal to the density.

12. If two cubic space lattices are placed the one within the other, so that the points of the one form the centres of the cubes of the other, that lattice is obtained which possesses the densest arrangement in the planes of the rhombic dodecahedron.<sup>1</sup> The points of this space lattice form the centres of **heptaparallelohedra** having the shape of a cubo-octahedron<sup>2</sup>; its volume is, naturally, the half of the corresponding hexahedron.

By a homogeneous deformation, resulting in the lengths of the three sides of the cube becoming unequally lengthened, this heptaparallelohedron passes into that mentioned under 6.

13. The space lattice which possesses closest packing in the octahedral planes, and which is formed from four simple cubic space lattices,<sup>3</sup> gives a space unit whose volume is only one-fourth of that of the simple cubic space unit, and whose shape is that of a rhombic dodecahedron having its three tetragonal axes equal in length to the edges of the circumscribed cube.

A homogeneous deformation by which only the length of one

<sup>1</sup> *Phys. Kryst.*, third edition, fig. 144 *b*; fourth edition, fig. 160 *b*.

<sup>2</sup> *Phys. Kryst.*, third edition, fig. 152; fourth edition, fig. 148.

<sup>3</sup> *Phys. Kryst.*, third edition, fig. 144 *c*; fourth edition, fig. 160 *c*.

of these axes is affected gives rise to the hexaparallelohedron mentioned under 9; whilst a deformation resulting in all three axes becoming unequal gives rise to that mentioned under 7.

14. A peculiar position is occupied by the **hexagonal** space lattice, in which the points lie at the corners of a trigonal prism. The lattice points form the centres of space units whose shape is that of a hexagonal prism. If the ratio of  $\omega$ , the height of this prism (the principal axis), to  $\chi$ , the distance between opposite corners of the base (a lateral axis), is expressed by  $c$ , it follows that

$$\chi = \sqrt[3]{\{V/c\}} / \sin 60^\circ$$

$$\omega = c\chi = \sqrt[3]{\{Vc^2\}} / \sin 60^\circ.$$

By a homogeneous deformation resulting in a slight lengthening or shortening in the direction of the normal to the front prism face, the hexagonal prism changes into the pseudo-hexagonal combination of a pinacoid and a prism with a basal plane, whose three diagonals are now no longer exactly equal; two of these have the same length, which may be designated by  $\chi$ , and make equal angles, of about  $30^\circ$ , with the axis of deformation; the third, whose length may be taken as  $\psi$ , is normal to the bisector of the angle between the other two. Such a space unit corresponds to the rhombic prismatic space lattice, and its dimensions can be easily calculated from the rectangular parallelepiped whose sides are in the same proportion as the crystallographic axes,  $a$ ,  $b$ ,  $c$ , and whose volume is double that of the former.

If the deformation axis is inclined to the normal of the front prism face of the hexagonal prism, but lies in the vertical plane, there results the pseudo-hexagonal monoclinic combination, analogous to the preceding one, and the calculation follows from the corresponding parallelepiped, as before, except that now the sides proportional to  $a$  and  $c$  form the oblique angle  $\beta$ . The ratio of the volume of this parallelepiped to the pseudo-hexagonal prism is unaffected by the homogeneous deformation.

If, lastly, the deformation of the hexagonal prism leads to the triclinic combination of three pairs of parallel planes intersecting at nearly equal angles, then the base has three unequal and unequally inclined diagonals  $\chi$ ,  $\psi$ , and  $\psi'$ . The calculation of these can be effected as before, by means of an analogous parallelepiped—in this case triclinic, however—whose volume is double that of the pseudo-hexagonal space unit.

Since the introduction of topic parameters in place of the crystallographic axial ratios has rendered it possible to compare with one another the corresponding dimensions of the crystal structures of different substances, we may now investigate whether in certain cases the change in the crystal structure, brought about by a chemical change, takes place in a particular direction, so that conclusions might be drawn therefrom regarding a definite mutual situation of the atoms in the crystal structure. Even from a comparison merely of the crystallographic axial ratios, it had previously been remarked<sup>1</sup> that often, on the substitution of hydrogen by some other univalent atom or radical, an alteration takes place only in a particular direction; this phenomenon was called **morphotropy**. At the same time, however, it remained uncertain whether the apparent increase in an axial ratio was not in reality due to a diminution of the other two. This uncertainty disappears on comparing the topic parameters of two substances, of which one is a substitution product of the other. The determination of the topic parameters, however, necessitates very accurate determinations of the densities of the crystallised substances which are to be compared, and such have become possible only in recent times by the improvement of methods, and especially by the introduction of what may be called the **free suspension method**, in which use is made of dense liquids.

That this method is the only one applicable to the accurate determination of the densities of crystallised substances, was shown by Retgers.<sup>2</sup> In the laboratory of the author it has been used in a comprehensive manner by Gossner for his investigations, and his results are reproduced in the following paragraphs:—

The nature of the suspension method is as follows: By suitable admixture of two liquids a third is obtained having the same

<sup>1</sup> P. Groth, "Über Beziehungen zwischen Krystallform und chemischer Constitution bei einigen organischen Verbindungen," *Berichte d. d. chem. Ges.* 1870, 3, 449.

<sup>2</sup> *Zeits. f. phys. Chem.* 1889, 3, 296; *Journ. C. S.* 56, 812.



density as the crystal under investigation, as shown by the latter remaining suspended in it, neither rising nor sinking. The density of the liquid is then determined.

Amongst dense liquids which are suitable for this purpose, when employed along with some other lighter one, there may be mentioned :—

1. **Acetylene tetrabromide**,  $C_2H_2Br_4$ .  $D. = 3.001$  at  $6^\circ C$ . Can be easily prepared by passing acetylene into cooled bromine.<sup>1</sup> Almost colourless, and very stable ; easily mobile.

2. **Thoulet's solution**. An aqueous solution of potassium mercuri-iodide ( $KI : HgI_2$  in the ratio  $1 : 1.239$ ) ; introduced by Thoulet,<sup>2</sup> and more fully investigated by V. Goldschmidt.<sup>3</sup> Almost colourless ; coefficient of expansion small ; hygroscopic ; somewhat viscous ; attacks the skin.

3. **Methylene iodide**,  $CH_2I_2$ .  $D. 3.33$ . Introduced by Brauns<sup>4</sup> ; its applicability was specially brought forward by Retgers.<sup>5</sup> Nearly colourless in pure state, but liable to decomposition ; easily mobile ; coefficient of expansion very large.

4. **Klein's solution**. An aqueous solution of cadmium borotungstate,  $2Cd(OH)_2.B_2O_3.9WO_3.16H_2O$ .  $D.$ , up to  $3.28$ . The salt itself melts in its water of crystallisation at  $75^\circ$ , and the density of the liquid thus obtained goes up to  $3.6$ .<sup>6</sup>

5. **Rohrbach's solution**. An aqueous solution of 100 parts barium iodide and 130 parts mercuric iodide.  $D.$ , up to  $3.588$ .<sup>7</sup>

Only the first, second, and third of these liquids are employed for chemico-crystallographical investigations ; the use of Klein's and Rohrbach's solutions is restricted to petrographical work.

Which of these three liquids is to be employed depends naturally, in the first instance, on the solubility of the substance to be investigated. Thoulet's solution is diluted with water ;

<sup>1</sup> Muthmann, *Zeits. f. Kryst.* 1899, 30, 73.

<sup>2</sup> *Bull. soc. min. fr.* 1879, 2, 17.

<sup>3</sup> *N. Jahrb. f. Min.* 1881, Beil.-Bd. 1, 179 ; *Zeits. f. Kryst.* 7, 306 ; *Journ. C. S.* 44, 159.

<sup>4</sup> *N. Jahrb. f. Min.* 1886, 2, 72.

<sup>5</sup> *Zeits. f. phys. Chem.* 1889, 3, 289 and 497 ; *Journ. C. S.* 56, 812 and 931.

<sup>6</sup> D. Klein, *Bull. soc. min. fr.* 1881, 4, 149 ; *Zeits. f. Kryst.* 6, 306 ; *Journ. C. S.* 40, 1168.

<sup>7</sup> Rohrbach, *Ann. d. Phys. u. Chemie*, N. F., 1883, 20, 169 ; *Zeits. f. Kryst.* 8, 422 ; *N. Jahrb. f. Min.* 1883, 2, 186 ; *Journ. C. S.* 44, 1060.

acetylene tetrabromide and methylene iodide, with benzene or toluene, less satisfactorily with xylene.

The degree of accuracy with which suspension may be arrived at depends on the viscosity of the liquid. Thoulet's solution is somewhat viscous, and, further, acts on the human skin, consequently methylene iodide, or, still better, acetylene tetrabromide, is to be preferred wherever possible. On exposure to light, methylene iodide liberates iodine and becomes dark coloured; it also acts chemically on many substances. Acetylene bromide, on the other hand, is a colourless liquid, which requires no purification even after prolonged use; as additional advantages are to be reckoned the low cost and the convenient method of preparation. It seems to be still more mobile than methylene iodide.

As regards the determination of the density of the suspending liquid, the method described by Retgers<sup>1</sup> is not very convenient.

The following method is rapid and accurate to a few units in the third decimal figure:—The liquid is prepared in a test tube, contact with the hand being avoided as far as possible. A large number of the purest crystal fragments obtainable are introduced, and the densest is ultimately brought into a state of suspension. The liquid is then quickly transferred to a suitable vessel, and its density determined by means of an accurate Westphal balance.

The temperature of the liquid is here of no moment, provided it is the same in the mixing and measuring vessels. With rapid working, and avoiding unnecessary contact with the operator's hands, this condition can be fulfilled with a fair degree of approximation.

It is necessary to state the temperature at which the density has been determined, unless it is to be tacitly assumed that the experiment was carried out at the ordinary laboratory temperature of 15°-20°. Retgers<sup>2</sup> has shown that with temperature differences amounting to 10°-15°, the variation in the density may already exceed the observational error.

Although a very short period has elapsed since a beginning was made with the determination, by the foregoing method, of the densities of substances undergoing crystallographical investigation, and consequently the

<sup>1</sup> *Zeits. f. phys. Chem.* 1889, 3, 289.

<sup>2</sup> *Zeits. f. phys. Chem.* 1889, 3, 307.

number of compounds which are suitable for the comparison of their topic parameters is still very limited, there have already been found cases in which substitution has produced a morphotropic change which has indubitably taken place in a particular direction, as the following examples will show :—

Ammonium iodide crystallises in cubes exhibiting perfect cubic cleavage, so that the regular space lattice constituting the foundation of the structure must be the simple cubic one. Since the density ( $d$ ) of the crystals is 2.501, and the molecular weight ( $M$ ) 143.83, the equivalent volume  $V$  is 57.51, which gives 3.860 as the side of the elementary parallelepiped. Slavík<sup>1</sup> has also investigated the compounds in which the four atoms of hydrogen are replaced by methyl, ethyl, and propyl groups. **Tetramethylammonium iodide** crystallises tetragonally, with perfect cleavage parallel to the two forms  $\{100\}$  and  $\{001\}$ , perpendicular to one another; evidently, therefore, it possesses a crystal structure which only differs essentially from that of ammonium iodide in having the dimensions parallel to the  $c$  axis different from those parallel to the two  $a$  axes. As shown in the table below, this difference has been brought about by a lengthening of the  $a$  axes, whilst the value of  $\omega$ , corresponding to the  $c$  axis, has undergone no noteworthy change. **Tetraethylammonium iodide** also crystallises tetragonally, but does not exhibit the complete pseudo-cubic cleavage of the methyl compound; that the salt nevertheless belongs to the same morphotropic series is shown by the regular progression of the equivalent volume for all three substances, and also by the regular increase of the dimensions  $\chi$  and  $\psi$ , whilst  $\omega$  has again undergone only slight diminution. Hence it is to be concluded that *the introduction of the methyl and ethyl groups into the crystal structure of ammonium iodide has taken place in one of the three cubic planes of the latter, which plane has thereby become the tetragonal basal plane.* The nitrogen atoms, for example, might be looked upon as occupying the centres of a cubic space lattice formed of iodine atoms, the hydrogen atoms being arranged between them on the four tetrahedron face normals; the carbon and hydrogen atoms replacing them would then all lie in a horizontal plane, and

<sup>1</sup> *Zeits. f. Kryst.* 1902, 36, 268 et seq.

this would necessitate the pushing apart of the iodine atoms in the four horizontal directions. If still larger alkyl groups are introduced, then their arrangement in a plane is no longer compatible with equilibrium, and there results an arrangement in space which leads to a difference in the two horizontal dimensions, and to a considerable pushing apart of the atoms vertically. Hand in hand with this there is an alteration in the equivalent volume, which no longer corresponds to that between the first members of the series. (See the propyl compound [rhombic] in the table below.)

	NH <sub>4</sub> I	$\Delta$	N(CH <sub>3</sub> ) <sub>4</sub> I	$\Delta$	N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> I	$\Delta$	N(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> I
V =	57.51	51.19	108.70	54.21	162.91	73.04	235.95
$\chi$ =	3.860	1.459	5.319	1.329	6.648	-0.555	6.093
$\psi$ =	3.860	1.459	5.319	1.329	6.648	1.103	7.851
$\omega$ =	3.860	-0.018	3.842	-0.156	3.686	1.247	4.933

Ammonium chloroplatinate, (NH<sub>4</sub>)<sub>2</sub> PtCl<sub>6</sub>, (cubic) always exhibits the octahedron as its predominating crystal form, and possesses perfect cleavage parallel to the faces of that form; consequently, an octahedral structure must be ascribed to it, with the rhombic dodecahedron for the shape of its space unit. (See page 42, No. 13.) From the equivalent volume,  $V=143.6$ , it follows that the side of the corresponding cube (possessing a volume four times that of the space unit) is  $\chi=\psi=\omega=8.313$ . If, now, one hydrogen atom in each NH<sub>4</sub> is replaced by methyl, the octahedron is replaced by a pronouncedly pseudo-octahedral form, constituted by a rhombohedron {111} with a less distinct cleavage, and a very perfect cleavage parallel to the basal pinacoid, {111}; the cube of ammonium chloroplatinate corresponds, in the case of methylammonium chloroplatinate, to a rhombohedron {100}, having  $a=79^\circ 5\frac{1}{2}'$ . By calculation from the equivalent volume,  $V=186.5$ , the side of this rhombohedron is found to have the value  $\chi=\psi=\omega=9.214$ . Whilst, therefore, the introduction of the two methyl groups has had the effect of causing a general pushing asunder of the atoms, the actual linear extension has taken place along one only of the four trigonal axes. *The deformation therefore corresponds to an arrangement of the methyl groups in one of the four trigonal axes* of the structure of the ammonium chloroplatinate. It is therefore to be expected that the substitution of all four hydrogen atoms of the ammonium radical by methyl groups should induce a similar expansion, but

equally so in all four of the trigonal axes. As a matter of fact, **tetramethylammonium chloroplatinate** is again cubic, and crystallises in octahedra with perfect octahedral cleavage, like the ammonium salt, and from its equivalent volume,  $V=304.4$ , the value  $\chi=\psi=\omega=10.678$  is obtained. That the space distribution of the methyl groups which have been introduced has taken place in a regularly progressive manner, appears from a comparison of the equivalent volumes; for the increase on passing from ammonium chloroplatinate to the monomethylammonium salt is approximately one-fourth of that on passing from the former to the tetramethylammonium salt. From what has just been stated it would be expected that the replacement of two hydrogen atoms in ammonium by methyl groups would lead to a deformation into a less symmetrical crystal structure. As a matter of fact, **dimethylammonium chloroplatinate** crystallises rhombic, but in two modifications, only one of which possesses an equivalent volume fitting approximately into the above series; this form exhibits cleavage parallel to a prism, which probably corresponds to that cleavage prism of the ammonium salt which would be constituted by two pairs of octahedral faces. On account of the polymorphism existing in this case, however, a closer comparison cannot be carried out with sufficient probability regarding the conclusions drawn; the same is the case for the trimethyl compound.

When **ethylammonium chloroplatinate** is compared with ammonium chloroplatinate, it becomes evident that the replacement of one atom of hydrogen in ammonium by an ethyl group gives rise to the production of an essentially different crystal structure; it appears from the properties of the only known modification of the ethyl compound that it does not represent the state corresponding to the above-mentioned methyl compound. The crystals, it is true, are apparently trigonal with a very perfect cleavage parallel to  $\{111\}$ , but the other faces corresponding to those of the octahedron, namely, those of the rhombohedron  $\{11\bar{1}\}$ , are never observed (nor are they on the isomorphous bromoplatinate nor on ethylammonium chlorostannate), and there is no cleavage parallel to them; the observed forms point rather to a hexagonal crystal structure (see page 43, No. 14). If the topic parameters of ethylammonium chloroplatinate are calculated in accordance with this assumption, we obtain:  $V=217.95$   $\chi=\psi=6.546$   $\omega=7.831$ .

This modification, which consequently does not correspond to the first described series derived from ammonium chloroplatinate, undoubtedly does correspond to the only known form of **propylammonium chloroplatinate**,<sup>1</sup> whose crystals, though monoclinic, nevertheless possess a pronouncedly pseudo-hexagonal character, with perfect cleavage parallel to the pseudo-hexagonal basal plane. If the dimensions are calculated on the assumption of a pseudo-hexagonal prism (see page 43) as the space unit of the crystal structure, with its basal plane making an angle of  $75^{\circ}33\frac{1}{2}'$  with the front prism face, then the following values are obtained for its topic parameters:

$$V = 236.11 \quad \chi = 6.307 \quad \psi = 6.528 \quad \omega = 9.227.$$

**Isopropylammonium chloroplatinate** belongs doubtless to the same morphotropic series, for it also is pronouncedly pseudo-hexagonal, with basal cleavage. The two polymorphous forms of this salt mentioned on page 9 have nearly identical angles, and the twinning plane of the lamellæ corresponds to a face of the pseudo-hexagonal prism. The topic parameters of this prism, whose base forms right angles with the side faces, are found to be as follows:

$$V = 234.95 \quad \chi = 6.314 \quad \psi = 6.585 \quad \omega = 8.829.$$

**Butylammonium chloroplatinate**, which exhibits a crystalline form very similar to the preceding one, is still more pronouncedly pseudo-hexagonal. For this substance the analogous calculation gives the values:

$$V = 274.39 \quad \chi = 6.467 \quad \psi = 6.623 \quad \omega = 9.945.^2$$

Hence it is evident that the homologous series beginning with the ethylammonium salt forms a regular morphotropic

<sup>1</sup> On the other hand, there exists a second modification of the analogous chloroplatinate, trigonal and with basal cleavage, whose crystal constants, however, are unknown; if this modification, in the case of propylammonium chloroplatinate, were obtainable in measurable crystals, it would doubtless prove to belong to the morphotropic series first described.

<sup>2</sup> The data regarding the substituted ammonium chloroplatinates are derived from the very complete investigations of J. A. Le Bel and A. Ries (*Zeits. f. Kryst.* 1902, **36**, 321 *et seq.*; and 1904, **39**, 49 *et seq.*). By these authors, however, the two last-mentioned salts are orientated in a manner different from that adopted here, the pseudo-hexagonal basal plane being taken as  $\{010\}$ .



series, since the dimensions of the hexagonal, or the pseudo-hexagonal, base experience only insignificant changes by the introduction of additional methyl groups, whilst the height of the corresponding prism, which constitutes the space unit of the crystal structure, increases about equally on changing from ethyl to propyl, and from propyl to butyl. This would therefore indicate that when the substitution takes place these groups are inserted in the direction of the hexagonal or pseudo-hexagonal axis; in further accordance with this view is the fact that, of the two propyl derivatives, it is the one which has the shorter carbon chain, *i.e.* the isopropyl compound, which exhibits the lower value for  $\omega$ .

The publications of Ries, already referred to, contain still other examples of this kind of relationship. Others were supplied by the investigation of G. Mez into the derivatives of carbamide,<sup>1</sup> from which what follows is extracted:—

**Carbamide or urea**,  $\text{CO}(\text{NH}_2)_2$ , crystallises tetragonal, and cleaves very perfectly parallel to  $\{110\}$ , less so parallel to  $\{001\}$ .

**Methylcarbamide** possesses rhombic symmetry, but exhibits an exceedingly perfect cleavage parallel to a nearly rectangular prism, and a perfect one parallel to  $\{001\}$ . Hence the relationship between the crystal structures of the two substances is so striking, that these must be looked upon as corresponding. A comparison of their topic parameters (see the following table) shows that the change in the dimensions is restricted essentially to the vertical direction. If a second methyl group is introduced on the same nitrogen atom, there results *as-dimethylcarbamide*, whose symmetry is monoclinic and which exhibits only one perfect cleavage. Although its relationships with the preceding compound are not so simple, comparison nevertheless shows that this substitution also has acted in a similar manner, since  $\omega$  has still further increased, whilst  $\chi$  and  $\psi$  are little changed (the mean values of  $\chi$  and  $\psi$  for the three substances are respectively 3.778, 3.695, and 3.581, showing a regular diminution).

	$\text{CO}(\text{NH}_2)_2$	$\text{CONH}_2\text{NHCH}_3$	$\text{CONH}_2\text{N}(\text{CH}_3)_2$
$V =$	44.94	61.46	70.12
$\chi =$	3.778	3.676	3.920
$\psi =$	3.778	3.713	3.241
$\omega =$	3.148	4.502	5.531

<sup>1</sup> *Zeits. f. Kryst.* 1902, 35, 242 et seq.

A totally different morphotropic effect, resulting from the introduction of the methyl group, is observed when the  $\text{CH}_3$  goes to the second nitrogen atom of methyl carbamide or of *as*-dimethylcarbamide; though the crystals of the two derivatives thus obtained, respectively rhombic and monoclinic, also have two parameters which differ but little from one another, these are the two larger ones, the third being considerably less.

**Metanitriline** crystallises rhombic; if its predominating prism is taken as  $\{110\}$ , then, adopting Schröder's determination of the density, we obtain

$$V = 95.9 \quad \chi = 5.181 \quad \psi = 3.479 \quad \omega = 5.318.$$

By introduction of a methyl group this substance gives rise to 1:2:4-nitrotoluidine, for which Jaeger<sup>1</sup> found the following values:

$$V = 111.8 \quad \chi = 5.424 \quad \psi = 3.882 \quad \omega = 5.670.$$

Here there appears to have taken place an all-round extension of the dimensions of the crystal structure; actually, however, the deformation has proceeded essentially in one particular direction, namely, along a diagonal of the plane (010) of the parallelepiped, which thereby has become converted into a monoclinic one.

The fact that in many cases the introduction of methyl for hydrogen brings about a definitely orientated alteration of the crystal structure, results in the crystals of homologous compounds often showing a similarity in the angles lying in certain zones. This phenomenon has attracted attention for some considerable time; in particular, Hiortdahl<sup>2</sup> demonstrated the existence of a series of such cases, and described the phenomenon as **partial isomorphism**. Since the more general treatment of the question regarding the alteration brought about by substitution,<sup>3</sup> a partial agreement between the crystallographic axial ratios of homologous substances has been proved in numerous examples. Of these there need only be mentioned the two series, derived, the one from formanilide,  $\text{C}_6\text{H}_5\text{NHCOH}$ , by

<sup>1</sup> *Zeits. f. Kryst.* 1903, 38, 89.

<sup>2</sup> *Journ. prakt. Chem.* 1865, 94, 286.

<sup>3</sup> 1870, Groth *loc. cit.*

replacement of the hydrogen of the COH group by methyl, ethyl, etc., the other from acetanilide,  $C_6H_5NHCOCH_3$ , by replacement of the hydrogen of the NH group by alkyl radicals. These have been investigated by Wilson,<sup>1</sup> but the results are not yet published in detail.

Experience has frequently shown that the introduction of the methyl group brings about an alteration of the symmetry of the crystal structure in the sense of diminishing it, as has already been shown by several cases among the examples given above. As regards the extent of this change, in general, we should expect, *a priori*, that it must be so much the less, the more preponderating the influence exercised on the crystal structure by the remaining constituents common to the two homologous substances. As a matter of fact, it has been proved by numerous examples that *the morphotropic effect of the methyl group is less, the larger the chemical molecule of the compound in which the substitution is carried out*. How slight the alteration produced by the introduction of the methyl group may be in the case of very large molecules is shown, for example, by a comparison of the methyl ester of phenaceturic acid,  $C_6H_5 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot COOCH_3$ , with the ethyl ester; both possess the same crystal habit and nearly identical angles. Similar behaviour is observed with the esters of naphthalene sulphonic acid,  $C_{10}H_7SO_3H$ , santonic acid, and others, in which the difference between the methyl and the ethyl esters is generally very slight, but that between the acid itself and the methyl ester is somewhat greater.

In the case of certain substances crystallising in the cubic system, no change whatever appears to take place on the substitution of methyl for hydrogen, *e.g.*, ammonium alum and trimethylammonium alum, ammonium chloroplatinate and tetramethyl ammonium chloroplatinate. It has already been shown on page 48, however, that although in such a case the forms of the crystals coincide, their structures do not, for the dimensions of the latter ex-

<sup>1</sup> *Rep., Brit. Assoc.*, 1900, 167,

perience a considerable increase by the introduction of the methyl groups. On this account, as will be shown later, two such homologous substances cannot well be described as *isomorphous*.

It is therefore evident that the relations between the crystal structures of substances in a homologous series can be recognised only by a comparison of the dimensions and angles of the space units on which the structures are based, and for this the requisite complete crystallographic and volumetric investigations (due attention being paid to the question of polymorphism) are still lacking for nearly all homologous series.

The same considerations apply to the determination of the morphotropic deformation which a crystal structure undergoes on the introduction of a halogen atom in place of a hydrogen atom. Even in connection with the first attempts in this direction, which were based merely on the coincidence of the angles of certain zones,<sup>1</sup> it was recognised that the morphotropic effect of the halogens is similar to that of the methyl group, and consequently the halogen derivative of a substance possesses in many cases a lower symmetry than the substance itself. Quite recently it has been pointed out by Jaeger<sup>2</sup> that this analogy is determined by the agreement, especially between Br and CH<sub>3</sub>, as regards the way in which they occupy space, with which also are connected certain analogies in the chemical behaviour of the respective substances. In the following paragraphs a number of examples are given illustrative of the morphotropic deformation due to the halogens:—

**1:2:4-Bromonitrophenol**,  $C_6H_3.OH.\overset{1}{N}O_2.\overset{4}{Br}$ , crystallises monoclinic, and possesses the following topic parameters:—

$$V=107.87 \quad \chi=8.612 \quad \psi=2.928 \quad \omega=4.758 \quad \beta=115^{\circ} 56'.$$

On the introduction of a chlorine atom in the sixth position

<sup>1</sup> Groth, *loc. cit.*

<sup>2</sup> *Zeits. f. Kryst.*, 1904, **38**, 597 *et seq.*

there results a substance which also crystallises monoclinic<sup>1</sup> with the parameters :

$$V=118.70 \quad \chi=6.204 \quad \psi=5.926 \quad \omega=3.552 \quad \beta=114^{\circ} 38'.$$

In this case the symmetry, it is true, has not been lowered, and  $\beta$  has retained almost the same value, but the alteration in the structure is nevertheless a very considerable one, since the value of  $\psi$  has been nearly doubled, while those of  $\chi$  and  $\omega$  have been considerably diminished.

**Acetanilide**,  $C_6H_5NHC_2H_5O$ , at ordinary temperatures possesses a metastable modification (probably monoclinic), and a stable rhombic modification ; so also does *p*-chloroacetanilide, and the two stable modifications appear to represent corresponding states, since they possess similar cohesion, in accordance with which, therefore, the crystals are to be orientated. This gives rise to the following topic parameters (see table), which show that, though the symmetry has remained unaffected by the introduction of the chlorine atom, the values of  $\chi$  and  $\psi$  have undergone a considerable change in opposite sense, while  $\omega$  has remained nearly unaffected. *o-p*-dichloroacetanilide according to Fels' investigations<sup>2</sup> is monoclinic, so that here the diminution of symmetry in the chemical molecule is associated with a similar change in the crystal structure. In this deformation only one of the three parameters, namely  $\chi$ , has been essentially changed, as shown by the following table :—

	Acetanilide.	<i>p</i> -Chloroacetanilide.	<i>o-p</i> -Dichloroacetanilide.
$V$	= 111.97	122.37	136.09
$\chi$	= 8.260	6.825	8.259
$\psi$	= 3.996	5.114	4.987
$\omega$	= 3.392	3.506	3.375

It would be interesting to continue this series by the investigation of *o-o-p*-trichloroacetanilide, etc. Of those substances which are derived from acetanilide by the introduction of chlorine into the acetyl group, only the dichloro compound has been measured. It crystallises in the monoclinic system, but, like acetanilide, possesses a perfect pinacoidal cleavage ; if this is here also taken as  $\{100\}$ , then the predominating form becomes  $\{011\}$ , with an angle of  $80^{\circ} 30'$ , whilst the corresponding form on acetanilide would have an angle of  $80^{\circ} 28'$  (calculated). A further comparison

<sup>1</sup> Gossner, *Zeits. f. Kryst.* 1904, 40, 81.

<sup>2</sup> *Zeits. f. Kryst.* 1900, 32, 386, 407.

is impossible, owing to the lack of a density determination for the chlorine compound.

The **benzoic acid** group would also be suitable for closer study. The crystals of this acid are pronouncedly pseudo-tetragonal, with a very large value for the parameter corresponding to the tetragonal principal axis, and it is rather remarkable that no cleavage takes place at right angles to this axis. Seeing that the density of the measured crystals was not determined, and that the existing determinations differ very greatly, this substance certainly requires further investigation as regards its crystal structure. The stable form of ***m*-nitrobenzoic acid** has retained the pseudo-tetragonal character and the lack of cleavage observed with benzoic acid, but possesses a much shorter principal axis. The calculation of the topic parameters of the two substances, which on the basis of old density determinations is only approximately possible, indicates (on the assumption of corresponding conditions of structure) that for the nitro-derivative the values of  $\chi$  and  $\psi$  are about one and a half times as large, whilst  $\omega$  is only about half as large, as for benzoic acid. Two **chloronitrobenzoic acids** are formed from the above-mentioned nitrobenzoic acid; these have been investigated by Jaeger,<sup>1</sup> and their topic parameters are:

$\text{C}_6\text{H}_3\text{Cl}^{\cdot 3}\cdot\text{NO}_2^{\cdot 5}\cdot\text{COOH}^{\cdot 1}$	$\chi = 3\cdot167$	$\psi = 2\cdot765$	$\omega = 16\cdot620$
$\text{C}_6\text{H}_3\text{Cl}^{\cdot 4}\cdot\text{NO}_2^{\cdot 5=3}\cdot\text{COOH}^{\cdot 1}$	$\chi = 5\cdot148$	$\psi = 4\cdot022$	$\omega = 6\cdot925$

The typically pseudo-tetragonal crystals of the 2 : 5 acid have nearly the same values of  $\chi$  and  $\psi$  as benzoic acid has, but have a still larger value for  $\omega$ , and correspondingly complete cleavage on {001}; compared with nitrobenzoic acid, they exhibit diminution of  $\chi$  and  $\psi$  and very marked increase of  $\omega$ . The 4 : 5 acid shows greater similarity of habit with nitrobenzoic acid, and differs from it in that  $\chi$  and, more especially,  $\omega$  have undergone a not inconsiderable increase, whilst  $\psi$  has experienced a slight diminution. The same observer has also investigated two isomeric **chlorobenzoic acids**, and found for them:

$\text{C}_6\text{H}_4\text{Cl}^{\cdot 2}\cdot\text{COOH}^{\cdot 1}$	$\chi = 5\cdot638$	$\psi = 8\cdot508$	$\omega = 2\cdot118$
$\text{C}_6\text{H}_4\text{Cl}^{\cdot 4}\cdot\text{COOH}^{\cdot 1}$	$\chi = 3\cdot697$	$\psi = 2\cdot902$	$\omega = 9\cdot662$

In both of these pairs of cases it is evident that the morpho-

<sup>1</sup> *Zeits. f. Kryst.*, 1903, **38**, 301.



tropic effect of chlorine is entirely different when it takes up different positions in the molecule; and it is found generally that *two (position-) isomeric derivatives of benzene possess essentially different crystal structures.*

An apparent exception to this rule has been found by Jaeger<sup>1</sup> in the case of the 1 : 2 : 4 : 6.- and 1 : 2 : 3 : 5-tribromotoluenes, whose crystalline forms and equivalent volumes are as closely similar as in the case of isomorphous substances. Since the dibromotoluenes (mostly liquids) have not been crystallographically determined, no evidence can be adduced as to how this relationship might be explained by the change produced in the crystal structure of the dibromo compounds by the introduction of a third bromine atom.

Coincidence of the angles lying in certain zones is shown by *m*-nitroacetanilide and *p*-bromo-*m*-nitroacetanilide, likewise by *p*-nitroacetanilide and certain of its halogen derivatives, but the available data are too incomplete to allow of regularities being recognised. Further interesting series would be supplied by the halogen derivatives of methyl-*p*-tolylsulphone,<sup>2</sup> which in part show very close relationships between their crystalline forms; also, the chloro and bromo substitution compounds of naphthalene tetrachloride, whose angles, according to the investigations of Hintze,<sup>3</sup> generally display very considerable similarities.

The observations so far recorded uniformly indicate that the morphotropic effect of the halogens possesses certain analogies with that of methyl, and that, like the latter, it becomes less evident the larger and more complex the chemical molecule in which the substitution occurs.

The similarity of the effect of chlorine, bromine, and iodine, on which the isomorphism of the halogen compounds depends, will be discussed later.

It appeared from numerous examples of aromatic substances<sup>4</sup> that the morphotropic effect of the nitro-group is less than that of methyl or the halogens, and consequently that, in cases where different states due to polymorphism are not involved, the close relationship of the nitro-

<sup>1</sup> *Loc. cit.*, p. 577.

<sup>2</sup> See *Zeits. f. Kryst.* 1892, 20, 604.

<sup>3</sup> Poggend, *Ann. d. Phys.* 1874, Erg.-Bd. 6, 177.

<sup>4</sup> Groth, *loc. cit.*

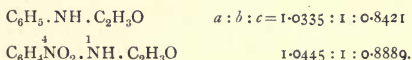
derivatives to the parent substance can be recognised immediately from the coincidence of the angles in a principal zone, *i.e.*, from the similarity of the ratios of two of the crystallographic axes. On that account these relationships could even be employed for the purpose of drawing conclusions of a chemical nature. In the year 1876 Hepp prepared a trinitrobenzene which was crystallographically examined by Friedländer,<sup>1</sup> when it was found that the compound exhibits morphotropic relationships, of the kind here referred to, with meta-dinitrobenzene, but not with either ortho- or para-dinitrobenzene; its nitro-groups must consequently occupy the positions 1.3.5, and the correctness of this conclusion has since been amply confirmed in other ways. These, and the other investigations on the nitro-derivatives of benzene and of phenol, and of their halogen substitution products, still require much supplementary work, however, and especially the provision of density determinations (which are almost entirely lacking) before the establishment of quantitative regularities will be rendered possible. Professor Körner, in Milan, to whom especially, as is well known, we owe the correct determination of the positions in these benzene derivatives, is engaged upon a comprehensive revision of this group of substances, simultaneously with which the complete crystallographical determination of the compounds will be carried on, so that we may expect to see, before very long, important advances in the recognition of the relations between crystal form and chemical constitution in the case of benzene derivatives. On that account, only a few examples will be mentioned in what follows, to illustrate the morphotropic rôle which is played by the nitro-group.

Whilst in many cases the crystal symmetry is not altered by the substitution of the nitro-group for hydrogen, in other cases it is lowered, especially when the symmetry of the chemical molecule is similarly affected. Such is the case, for example, with the monoclinic *p*-dibromobenzene; this, on the introduction of a nitro-group,

<sup>1</sup> *Zeits. f. Kryst.* 1879, 3, 168,

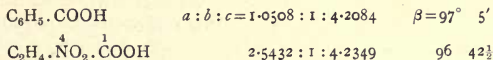
gives rise to a triclinic form whose prism zone, however, possesses almost exactly the same angles as the prism zone of the original substance.

An illustration of the symmetry of the crystal structure remaining unchanged when the symmetry of the chemical molecule also remains as before, is provided by acetanilide and *p*-nitroacetanilide, which both crystallise in the rhombic system. As we have here to deal with somewhat large chemical molecules, the entrance of the nitro-group effects only a moderate change, so that, when the two substances are so orientated as to have their pronounced cleavages coincident, their crystallographic axial ratios become very similar, especially if the predominating prism on acetanilide is taken as {110} :



When, on the other hand, the nitro-group takes up the less symmetrical meta position in acetanilide, the symmetry of the crystal structure becomes monoclinic ; nevertheless, its relation to that of acetanilide remains a very intimate one, for, assuming the perfect cleavage here to be orientated in the same way as the plane of perfect cleavage in acetanilide, {100}, the bipyramidal combination {111} {111} of the nitro-derivative represents simply the rhombic pyramid, occurring on the other substance, deformed into a monoclinic one ; *i.e.*, if, inversely, that monoclinic combination were subjected to a homogeneous deformation such that it attained rhombic symmetry, there would then result a form with angles very similar to those exhibited by the solitary bipyramid observed on acetanilide.

The series of **nitrobenzoic acids** is more completely known—not their densities, however. From a comparison of the following crystallographic axial ratios



it appears probable that by the entrance of a nitro-group into the para position, whereby the symmetry has not been affected, a change has taken place only along the direction of the *a* axis. The morphotropic effect of the nitro-group is quite different, however, when this takes up either of the other positions, whereby the

symmetry of the chemical molecule also is diminished. **Orthonitrobenzoic acid** is triclinic, and forms tabular crystals whose predominating lateral faces make an angle of  $69^\circ 0'$  with the tabular face ( $a:b$ , according to Haushofer), whilst the corresponding angle ( $c:d$ ) of benzoic acid is  $69^\circ 24'$ . (The comparison cannot be carried further, because the elements of *o*-nitrobenzoic acid are not completely known). **Metanitrobenzoic acid**, according to Bodewig, exists in three modifications, of which the stable one has a prism angle of  $87^\circ 48'$ , whilst for benzoic acid the angle  $(110):(110)$  is  $87^\circ 36'$ ; both substances are monoclinic, but an alteration in the symmetry has taken place here also, for the form  $\{001\}$ , which predominates in each case, is in the one inclined in the plane  $(010)$ , and in the other in the planes  $(100)$ . Of the **dinitrobenzoic acids**,

the compound  $C_6H_3(NO_2)_{2.4}^1.COOH$  is known in two modifications, of which the stable one exhibits an unmistakable relation to paranitrobenzoic acid; both possess perfect cleavage on  $\{101\}$ , the angle  $\beta$  amounts to  $96^\circ 42\frac{1}{2}'$  and  $97^\circ 21'$  respectively, and the ratio  $a:c$  is likewise similar in both cases, so that the alteration due to the entrance of the second nitro-group seems to be confined essentially to the axis  $b$ . Owing to our incomplete knowledge of orthonitrobenzoic acid, the relations of the dinitro acid to it cannot be determined. On the other hand, those of the acid

$C_6H_3(NO_2)_{2.5}^1.COOH$  to metanitrobenzoic acid (the only mononitro acid from which the former can be derived by introduction of the nitro-group) are very distinct: habit and cleavage are the same in the two substances, and the axial ratios:

Metanitrobenzoic acid	$a:b:c=0.9656:1:1.2327$	$\beta=91^\circ 11'$
Metadinitrobenzoic acid	$1.1191:1:1.1294$	$96^\circ 23.$

show that the morphotropic effect is now no longer a very pronounced one. If, finally, the two nitro-groups are introduced into the benzoic acid molecule so that they replace the two hydrogen atoms neighbouring to the carboxyl group, then the crystalline form of the acid becomes rhombic with the axial ratios  $a:b:c=0.817:1:2.305$ , whilst the habit of the crystals exhibits the greatest similarity with orthonitrobenzoic acid and benzoic acid itself.

**Trinitrobenzoic acid**,  $C_6H_2(NO_2)_{2.4.6}^1.COOH$ , possesses the same symmetry as the preceding compound; it crystallises rhombic,

with the axial ratios  $a:b:c=0.8757:1:0.5005$ , and its predominating prism  $\{101\}$  exhibits angles similar to those of the corresponding faces  $(101)$  and  $(10\bar{1})$  of paranitro-benzoic acid.

An example illustrating that with still larger chemical molecules the change caused by the entrance of the nitro-group becomes still less marked, is supplied by the nearly complete coincidence of crystal structure shown by tri- and tetra-nitro-*p*-azotoluene.<sup>1</sup>

For a study of the morphotropic effect of the amido-group there does not at present exist any sufficient material in the form of crystallographical investigation.

As regards the hydroxyl group, on the other hand, it was pointed out by the author, as far back as 1870, that its introduction into benzene in the place of the hydrogen did not affect the symmetry, and modified the dimensions only in one particular direction. As a matter of fact, investigations instituted since then have shown that the morphotropic effect of hydroxyl in aromatic compounds presents certain analogies with that produced by the nitro-group. A few examples may serve to illustrate the relationships arising in connection with this substitution.

A comparison may be made between *m*-dinitrobenzene and two dinitrophenols derived from it by the introduction of hydroxyl:

$\text{C}_6\text{H}_4(\text{NO}_2)_2$	rhombic	$a:b:c=0.2855:1:0.5302$
$\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{OH}$	"	$0.4487:1:0.5278$
$\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{OH}$	monoclinic	$0.2972:1:0.5552 \quad \beta=106^\circ 20'$

In the one case, therefore, there is retention of the symmetry, and alteration along one axis, and in the other case the axial ratios remain almost unaffected whilst a lower symmetry results from the deformation. Here, in the meantime, only the relative changes can be determined, but in the following example it is possible to determine the topic parameters themselves.

<sup>1</sup> Zepharovich, *Zeits. f. Kryst.* 1889, 15, 218.

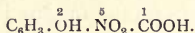
The symmetrical trinitrobenzene mentioned on page 58 has recently been more fully investigated by Peruzzi in the laboratory of the author, on material obtained by Koerner, as has also the symmetrical trinitrophenol (picric acid), which has already been repeatedly measured; and accurate density determinations of both have been carried out by Gossner. By means of crystallisations rich in faces, obtained at different temperatures and from different solvents, the fundamental form of both of these substances, which crystallise rhombic, could be deduced with a great degree of probability.

The following values were obtained :—

$\text{C}_6\text{H}_3(\text{NO}_2)_3$ <sup>1.3.5</sup>	$V = 125.31$	$\chi = 5.374$	$\psi = 5.665$	$\omega = 4.116$
$\text{C}_6\text{H}_2(\text{NO}_2)_3.\text{OH}$ <sup>1.3.5</sup>	$128.41$	$4.917$	$5.074$	$5.147.$

A comparison of these shows that the deformation consists in a marked increase of  $\omega$ , combined with a slight contraction in the directions of  $\chi$  and  $\psi$ .

Still less marked are the changes which are brought about by the introduction of the hydroxyl group into the benzoic acid molecule, with formation of salicylic acid; and also into that of *m*-nitrobenzoic acid with formation of the acid



In both cases we have to deal with monoclinic substances whose crystal symmetry is not changed by the substitution; in the first case there is a dimensional alteration, but only in one direction; in the second case there are, all over, only relatively small alterations.

Naphthalene,  $\text{C}_{10}\text{H}_8$ , crystallises monoclinic, as do also  $\alpha$ - and  $\beta$ -naphthol,  $\text{C}_{10}\text{H}_7\text{OH}$ ; both isomers possess a crystal habit coinciding with that of naphthalene, and the angles of all three are so much alike that they have been stated to be "isomorphous."

The results of the very incomplete investigations so far made regarding the influence which the substitution of hydrogen by methyl, chlorine, bromine, iodine, the nitro-group, and hydroxyl, exercises on the crystal structure, may be summed up in the following statements :—



*In many cases the alteration demonstrably takes place in definite directions, so that it is possible to draw therefrom conclusions regarding the arrangement of the atoms in the regular structure.*

*The nature and extent of the deformation depend not only on the nature of the substituting constituent (atom or radical), and on the crystal structure of the substance in which the substitution takes place, but also :*

- 1. On the position occupied by the replaced hydrogen atom in the chemical molecule (consequently isomeric substances possess different crystal structure) ; and*

- 2. On the size of the chemical molecule, since the alteration of the crystal structure in general becomes less, the more complex the composition of the compound in which the chemical change under consideration takes place.*

Similar relationships are recognisable on comparing the crystallographical properties of acids and those of their salts, which would indicate that the morphotropic effect of metals, on their introduction into the molecule of the acid in place of hydrogen, is subject to similar regularities. Since the majority of inorganic acids cannot be subjected to crystallographical investigation, such comparisons can be undertaken almost exclusively with organic acids, and even with these there is often no direct relationship observable, evidently because in such cases the change produced by the substitution is too radical a one. Here again, the relationships are much more distinctly recognisable in the case of the benzene derivatives, especially with the potassium and ammonium salts of the more complicated aromatic acids, amongst which there occur many stable substances which crystallise in the anhydrous state, and so are suitable for comparison. Since the present problem has as yet been the subject of no systematic treatment, it is in the meantime possible to give only such isolated examples as have been

discovered more or less accidentally in the course of crystallographical investigations.

According to Fock, **amidosulphonic acid**,  $\text{NH}_2\text{SO}_3\text{H}$ , crystallises rhombic, as does also its potassium salt; the following are their axial ratios, and it will be observed that  $a$  and  $b$  exhibit a striking agreement:

$\text{NH}_2\text{SO}_3\text{H}$	$a : b : c = 0.9948 : 1 : 1.1487$
$\text{NH}_2\text{SO}_3\text{K}$	$0.9944 : 1 : 0.7097.$

In the case of **tartaric acid** and its ammonium salt (the latter investigated by Wyruboff), determinations of the densities are available, so that their topic parameters can be given; they both crystallise monoclinic:

	V	$\chi$	$\psi$	$\omega$	$\beta$
$(\text{CH}.\text{OH})_2(\text{COOH})_2$	84.52	5.142	4.034	4.141	$79^\circ 43'$
$(\text{CH}.\text{OH})_2(\text{COONH}_4)_2$	114.17	4.727	4.113	5.878	$87^\circ 35'$

The deformation, therefore, consists essentially in an increase in  $\omega$ .

**Glutamic acid** crystallises rhombic, its acid sodium salt monoclinic, but both exhibit a very closely agreeing ratio  $b : c$ :

$\text{COOH}(\text{CH}_2)_2.\text{CHNH}_2.\text{COOH}$	$a : b : c = 0.687 : 1 : 0.855$
$\text{COOH}(\text{CH}_2)_2.\text{CHNH}_2.\text{COONa}$	$1.013 : 1 : 0.864 \quad \beta = 97^\circ 59'.$

With **picric acid** and its potassium salt, which both crystallise rhombic, the dimensions of the space units can be directly compared; they are:

$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$	$V = 128.41$	$\chi = 4.917$	$\psi = 5.074$	$\psi = 5.147$
$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK}$	144.43	6.521	4.548	4.868.

The deformation due to the entrance of the potassium atom consists, therefore, in a considerable dilation in the direction of  $\chi$ , and a slight contraction in the plane at right angles thereto. This somewhat stable plane is simultaneously the one parallel to which the crystals of both substances generally exhibit tabular development. From this it may be assumed with considerable probability that, in the space unit of the crystallised acid, the hydroxyl occupies such a position that the potassium atom entering in place of hydrogen must produce a pushing asunder of the remaining atoms in the direction normal to that plane.

Similar relationships seem to exist between **benzoic acid** and **phenylglycollic acid** on the one hand and their ammonium salts on

the other, but these cases require fuller investigation. The same remark applies to **phthalic acid** and the acid sodium phthalate, which exhibit a very great similarity in their axial ratios, so that, corresponding to the large size of the chemical molecule, the entrance of the sodium can have caused only a moderate alteration in the dimensions of the crystal structure.

## ISOMORPHISM

### A. Similarity of Crystal Structure in Substances possessing Analogous Chemical Constitution

At the end of the previous section attention was called to the fact that, as regards crystal structure, the sodium salt of phthalic acid exhibits an intimate relationship with the acid itself. The corresponding salts of potassium, rubidium, caesium, and ammonium crystallise very like the sodium salt, and it is therefore to be assumed that the alteration in the crystal structure of phthalic acid, which results from the substitution of one or other of the above metals for hydrogen, in each case takes place in the same direction and is similar in extent ; on this ground, therefore, the analogously constituted salts of these metals must possess crystal structures whose space units are characterised not only by like symmetry, but also by nearly the same linear dimensions and, consequently, nearly the same volume. For this it is evidently necessary that, in the first place, the elements concerned should be capable of playing an analogous rôle in the chemical molecule, and this, as a matter of fact, is the case with the above-mentioned metals and ammonium. The differences in the dimensions of the space units of the individual salts of such a series, being brought about by the lack of equality in the space occupied by the atoms of the different metals in the crystal structure,

must, therefore, appear most marked in that direction in which the principal alteration of the crystal structure of the acid takes place. If, now, we compare the crystallographic axial ratios of the phthalates of sodium, potassium, rubidium, cæsium, and ammonium, we find not inconsiderable differences in the values of  $a$  and  $c$  ( $b$  being taken as unity), while the ratio  $a : c$  differs only slightly in the different members of the group. It is, therefore, to be presumed that the former differences depend on corresponding differences in the value  $\psi$  (corresponding to  $\delta$ ), and that it is in this direction that the principal deformation of the crystal structure of the acid takes place on the introduction of the metals under consideration.

This is in agreement with the fact that, in the case of the rubidium and cæsium salts, whose densities are known, the greatest difference in the topic parameters is that affecting the value of  $\psi$ , corresponding to the  $\delta$  axis.

The 1 : 2 : 4-bromonitrophenol mentioned on page 54 provides a case where the relations which the crystal structures of several analogous derivatives bear to the crystal structure of the substance from which they are jointly derived, can be directly recognised by a comparison of the topic parameters. In this crystal structure the introduction of chlorine into the sixth position produced the greatest change in the value of  $\psi$ , and the least in the value of  $\omega$ ; bromine and iodine behave in an entirely analogous manner when they replace the same hydrogen atom (6), as is evidenced by the following table of the topic parameters of the three substances (according to Gossner's investigation<sup>1</sup>):—

	V	$\chi$	$\psi$	$\omega$	$\beta$
$\text{C}_6\text{H}_2\text{.OH.}^1\text{NO}_2\text{.}^2\text{Br.}^4\text{Cl}^6$	118.7	6.204	5.926	3.552	114° 38'
$\text{C}_6\text{H}_2\text{.OH.}^1\text{NO}_2\text{.}^2\text{Br.}^4\text{Br}^6$	121.1	6.207	6.025	3.562	114 37
$\text{C}_6\text{H}_2\text{.OH.}^1\text{NO}_2\text{.}^2\text{Br.}^4\text{I}^6$	129.0	6.413	6.167	3.578	114 14

When these values are compared it is seen that the greatest difference (percentage as well as actual) occurs with

<sup>1</sup> *Loc. cit.*

$\psi$ , and the least with  $\omega$ ; *i.e.*, those directions in which respectively the greatest and the least change results in the crystal structure of bromonitrophenol when a halogen atom is introduced in place of hydrogen (see page 55). The three analogous derivatives form a progressive series as regards the habit of their crystalline form and the dimensions of their space units, so that here a higher atomic weight for the substituting element carries with it the occupation of a greater space as measured in all three directions.

Such a series, progressing with the atomic weight of the substituents, may often be recognised merely on comparison of the angles, as in the cases of the chloro- and bromo-derivatives of hydroquinone and of phenylpropionic acid.<sup>1</sup> Here again, however, demonstration of the prevailing regularities is placed beyond doubt only by a comparison of the topic parameters, for which purpose these were first introduced (see page 38).

The most comprehensive and exact investigations of such series of analogously constituted and similarly crystallised substances, are those of A. E. Tutton on the normal sulphates of potassium, rubidium, and cæsium,<sup>2</sup> the corresponding selenates,<sup>3</sup> and the double sulphates and selenates of these univalent metals with bivalent ones.<sup>4</sup>

By these masterly researches the proof has been supplied that, in the salts named, the replacement of potassium by rubidium, and of this by cæsium, brings about a change in the geometrical and physical properties of the respective crystals, which change progresses with the atomic weights of the metals, so that in the case of the rubidium salt the value for any property always lies between the values for the same property in the corresponding potassium and cæsium salts. The following table contains the dimen-

<sup>1</sup> Fels, *Zeits. f. Kryst.* 1900, **32**, 396-8.

<sup>2</sup> *Journ. C. S.* 1894, **65**, 628; 1896, **69**, 495; *Zeits. f. Kryst.* **24**, 1; **37**, 252.

<sup>3</sup> *Journ. C. S.* 1897, **71**, 846; *Zeits. f. Kryst.* **29**, 63.

<sup>4</sup> *Journ. C. S.* 1893, **63**, 337; 1896, **69**, 344; *Proc. Roy. Soc.* 1900, **66**, 248; 1901, **68**, 322; *Zeits. f. Kryst.* **21**, 491; **27**, 113, **33**, 1; **35**, 529.



sions of the space units for the normal sulphates and selenates, the crystal structure being referred to a rhombic space lattice, which, however, differs extraordinarily little from a hexagonal one ; the space unit is here taken as a pseudo-hexagonal prism (see page 43) whose height corresponds to the correct position of the crystal as given by Federow, and is equal to  $2c$ , as taken by Tutton).

	V	$\chi$	$\psi$	$\omega$
$K_2SO_4$	64.92	4.464	4.491	4.997
$Rb_2SO_4$	73.36	4.634	4.664	5.237
$Cs_2SO_4$	84.64	4.846	4.885	5.519
$K_2SeO_4$	71.71	4.636	4.662	5.118
$Rb_2SeO_4$	79.95	4.785	4.826	5.346
$Cs_2SeO_4$	91.16	4.987	5.035	5.697

As is seen, in both series the increase in all the topic parameters progresses with the increase in the atomic weights. Further, the sulphate of any one of the three metals stands in the same relation to the corresponding selenate, only here the replacement affects the acid-forming element and not the metal. In order to show clearly that a similar increase in the dimensions of the space unit takes place on the replacement of one of these elements by one of higher atomic weight, the following table is given containing, in addition to the above, the data for potassium chromate (which also shows the same crystal character) as calculated by Gossner from Mitscherlich's measurements and his own density determination.

	V	$\chi$	$\psi$	$\omega$
$K_2SO_4$	64.92	4.464	4.491	4.997
$K_2CrO_4$	70.39	4.600	4.647	5.088
$K_2SeO_4$	71.71	4.636	4.662	5.118

As already stated, those compounds which, in consequence of the similarity in the morphotropic effect of related elements, show a very close agreement in their crystal structure, are called **isomorphous substances**, and the elements concerned are said to "replace one another iso-

morphously." For example, the isomorphous replacement of chlorine by bromine depends, as was shown on page 67, on the nature of the change which the two elements produce in the crystal structure of a compound when each is introduced into that compound. Since, however, this change depends also on the nature of the compound in which the substitution takes place, it follows that the variation in the effect of the two substitutions (*i.e.*, the extent of the differences which are exhibited by the two resulting substances) will change with the type of compound, and in general will be smaller, the slighter the morphotropic effects of the elements themselves in that particular case.

The higher the degree of coincidence in the crystal structures of two isomorphous substances, the greater the coincidence to be expected with regard to the polymorphism which they exhibit. Two substances which are capable each of existing in two different modifications, these corresponding in pairs and standing in isomorphous relationship, are said to be **isodimorphous**. The limiting temperatures of stability for the two modifications are always different. For example, it is found that on passing from a chlorine to a bromine derivative, and, still more, from the latter to an iodine derivative, the melting point is as a general rule higher, and there is also a corresponding displacement of the temperature limits of stability for the different states. Therefore it often happens that the iodine compound (and not infrequently even the bromine compound) crystallises at ordinary temperatures in a modification which is different from that of the chlorine compound; and that the modification corresponding to the latter is produced only at higher temperatures. In all series of inorganic and organic substances there are examples of this, sufficient to justify the assumption that chlorine, bromine, and iodine always replace one another isomorphously, and that, in all cases in which similar compounds of these elements are not isomorphous, this difference is due to polymorphism. If, on the other hand, we compare with these elements the first

member of the halogen group, namely fluorine, we find that its simpler compounds differ greatly from those of chlorine, bromine, and iodine, even in their volume relationships, and as a rule present other differences in crystal structure. It is only when the molecule of the substance in which the halogen substitutions are affected is very great, and the change brought about by the substitution is consequently very slight, that there follows, as a natural consequence, so close an agreement between the fluorine compound and the others that the former displays the properties of a substance isomorphous with the latter. Fluorine, therefore, as regards isomorphous replacement, shows itself to be less closely related to chlorine than this is to bromine; and, as is well known, such is also the case with regard to its chemical character. In all groups of the periodic system of the elements, this applies generally to the relations between the first member and the next one, as will appear from the following short survey, in which are collected the principal facts hitherto observed regarding the replaceability of the individual elements, these being arranged in groups of like valency. Regarding the case of hydrogen, which is omitted from the review, it has already been shown that its replacement by a univalent metal produces a change which is less and less marked the larger the molecule of the acid in which the replacement takes place. Hence it is evident that in acids of an extraordinarily complex nature (as, for example, silicotungstic acid,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ ), the replacement of hydrogen by a univalent metal may exercise so slight an influence that the salt and the acid behave like isomorphous substances; likewise in many complex natural silicates, isomorphous replacement of the alkali metals and hydrogen must be assumed.

**I. Group of the alkali metals and of the univalent heavy metals.**—Lithium chloride,  $\text{LiCl}$ , and sodium chloride,  $\text{NaCl}$ , both crystallise cubic, but have such widely different equivalent volumes that they cannot be considered as isomorphous. The periodates of these metals,  $\text{LiIO}_4$  and  $\text{NaIO}_4$ , possess similar tetragonal forms,

but the sulphates,  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ , exhibit no sort of agreement. Only in the case of somewhat more complicated compounds does isomorphous replacement really begin; thus, the following salts are isomorphous: the dithionates,  $\text{Li}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ; the manganophosphates,  $\text{LiMnPO}_4$  and  $\text{NaMnPO}_4$ ; the double tartrates with thallium,  $\text{LiTlC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$  and  $\text{NaTlC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ; and others. As is well known, lithium, sodium, and potassium differ from one another in that the salts of the first two often crystallise with water of crystallisation, those of potassium, on the other hand, without it, so that they are not comparable with the former. When, however, all three metals form salts which are anhydrous, or possess the same quantity of water of crystallisation, it is found that the metals do not replace one another isomorphously in all of the simpler compounds, such as the chlorides, bromides, iodides, and azides, the chlorates, bromates, iodates, and all the simple carbonates, sulphates, and chromates; even in the case of some of the less simple compounds, such as the double magnesium sulphates,  $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , and the chloraurates,  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{KAuCl}_4 \cdot 2\text{H}_2\text{O}$ , true isomorphism is absent. The following, on the other hand, exhibit agreement in crystallographic character: the double carbonates,  $\text{Na}_2\text{K}_2(\text{CO}_3)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{Na}_3\text{K}(\text{CO}_3)_2 \cdot 12\text{H}_2\text{O}$ ; the alums,  $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ; the monohydrogen phosphates,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NaKHPO}_4 \cdot 7\text{H}_2\text{O}$ ; also the phthalates,  $\text{Na}_2\text{C}_8\text{H}_4\text{O}_4$  and  $\text{K}_2\text{C}_8\text{H}_4\text{O}_4$ , and the *o*-toluenesulphonates,  $\text{NaSO}_3\text{C}_7\text{H}_6$  and  $\text{KSO}_3\text{C}_7\text{H}_6$ ; whilst the *m*-dinitrobenzoates,  $\text{NaC}_7\text{H}_3\text{O}_2(\text{NO}_2)_2$  and  $\text{KC}_7\text{H}_3\text{O}_2(\text{NO}_2)_2$ , are not isomorphous. In complicated natural silicates also, lithium and sodium exhibit distinct differences from potassium (in the tourmalines, for example), whilst in others (such as vesuvianite), potassium, sodium, lithium, and hydrogen may vicariously represent one another. The difference of character between sodium and potassium is further exhibited by the fact that in some salts they occur side by side as constituents in definite atomic proportions, as in glaserite,  $\text{NaK}_3(\text{SO}_4)_2$ , and the double tartrate (Rochelle salt),  $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ ; the same is seen with lithium and potassium (in the double sulphate,  $\text{LiKSO}_4$ ; double racemate,  $\text{LiKC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ ; and others).

On the other hand, the isomorphous replacement of potassium, rubidium, and caesium is quite general, in simple compounds as in complex. Thus, their halides, nitrates, iodates, sulphates (see page 69), and selenates—both single and double salts—are com-

pletely isomorphous, as are also the respective salts of the most widely varying organic acids (see, for example, page 66). Only in a few cases do apparent exceptions arise, owing to the salts being polymorphous; thus, one particular modification of, say, the potassium salt, may be known, whilst in the case of the rubidium or caesium salt only some other modification may be known, owing to the different situation of the transition temperature. Ammonium behaves chemically exactly like an alkali metal, and accordingly the ammonium salts are generally isomorphous with the analogous potassium, rubidium, and caesium salts; in the case of the sulphates, it was shown by Tutton that the crystallographic and physical constants of the ammonium compounds lie between those of the rubidium and caesium compounds, but very near to the former, and in other isomorphous groups similar conditions seem to apply. On the other hand, the limiting temperatures of stability of a particular polymorphous modification are, in the case of the ammonium salt, often strikingly different from those for the potassium salt, and on this ground it very often happens that in the case of analogous compounds the potassium salt is observed in a different crystalline form from the ammonium salt. How, in such cases (*e.g.*, the acid sulphates, the chlorides, and the thiocyanates), the proof of the isodimorphism of the salt group is furnished, will be indicated in one of the following sections ("Isomorphous Mixtures"). For the isomorphism of the salts of univalent thallium with the corresponding potassium salts, there are numerous examples also, such as: the azides,  $\text{TlN}_3$  and  $\text{KN}_3$ ; the nitrates,  $\text{TlNO}_3$  and  $\text{KNO}_3$ ; the periodates,  $\text{TlIO}_4$  and  $\text{KIO}_4$ ; various sulphates, chromates, selenates, and particularly the corresponding double sulphates; finally, the oxalates, racemates, picrates, and others.

The univalent metals, copper, silver, and gold, in the form of the crystallised elements, constitute an undoubtedly isomorphous group, and the first two also replace each other isomorphously in a number of native sulphur compounds, as also in the following complicated salts: the triple thiocyanates,  $\text{Cs}_3\text{SrCu}_2(\text{SCN})_7$  and  $\text{Cs}_3\text{SrAg}_2(\text{SCN})_7$ ; and the compounds  $\text{NH}_4\text{Cl}, \text{CuCl}_4(\text{NH}_4)_2\text{S}_2\text{O}_3$  and  $\text{NH}_4\text{Cl}, \text{AgCl}_4(\text{NH}_4)_2\text{S}_2\text{O}_3$ . The non-similarity of other compounds of these metals (for example, the relatively simple double cyanides  $\text{KCu}(\text{CN})_2$  and  $\text{KAg}(\text{CN})_2$ ) may possibly be due to polymorphism. Sodium, as regards isomorphism, exhibits very close relations with silver. This is particularly noticeable with the chlorides, nitrates, iodates, sulphates, and dithionates, but

the question of the isomorphous replacement of these two metals requires further investigation.

**II. Group of the bivalent metals.**—Beryllium, in agreement with magnesium and zinc, crystallises hexagonal, and further, the form of beryllium oxide exhibits certain analogies with that of zinc oxide ; nevertheless an isomorphous replacement of beryllium by other bivalent metals in analogous salts has been found only in few cases. Beryllium aluminate and chromite,  $\text{Be}(\text{AlO}_2)_2$  and  $\text{Be}(\text{CrO}_2)_2$ , crystallise differently from the magnesium salts,  $\text{Mg}(\text{AlO}_2)_2$  and  $\text{Mg}(\text{CrO}_2)_2$ , whilst the double phosphates,  $\text{NaBePO}_4$  and  $\text{NaMnPO}_4$ , exhibit very similar forms. In some other phosphates, as, for example, the mineral groups of wagnerite,  $\text{MgMgFPO}_4$ , and herderite,  $\text{CaBeFPO}_4$ , more intimate relations between beryllium and the other bivalent metals may be recognised. Among the silicates, only phenacite,  $\text{Be}_2\text{SiO}_4$ , and willemite,  $\text{Zn}_2\text{SiO}_4$ , are comparable, because the salts of other metals, corresponding in composition to the remaining beryllium silicates (and therefore potentially isomorphous with them) are unknown. Further, there exist no normal beryllium salts of the fatty acids.

Very many groups of analogously constituted salts of the bivalent metals magnesium, manganese, iron, nickel, cobalt, zinc, and cadmium, derived from the most various acids, organic as well as inorganic, have been crystallographically determined ; with these it is regularly found that there is a very complete isomorphism of all the members of any such group. The same applies to the hydroxides, and also, to a certain extent, to the elements themselves. In the few cases in which apparent exceptions to this rule are found, as with magnesium sulphate and ferrous sulphate, it can be shown beyond doubt that the respective salts are isodimorphous (see under "Isomorphous Mixtures," page 91). Bivalent copper in the simpler compounds appears to stand apart from the above-mentioned metals, but in more complex salts it takes its place beside them ; thus the fluosilicate,  $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ , is isomorphous with the corresponding salts of magnesium, manganese, iron, nickel, cobalt and zinc ; also the fluozirconate,  $\text{Cu}_2\text{ZrF}_8 \cdot 12\text{H}_2\text{O}$ , with that of zinc ; the sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and double sulphate,  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , with those of magnesium, manganese, iron, cobalt, zinc, and cadmium ; but whilst the double sulphates of the other metals agree very closely among themselves as regards their angles, the copper salt in this respect stands distinctly apart. Further examples are supplied



by: the basic arsenate,  $\text{Cu}_2\text{OHAsO}_4$ , isomorphous with the zinc salt,  $\text{Zn}_2\text{OHAsO}_4$ ; the acid arsenate,  $\text{CuHAsO}_4\cdot\text{H}_2\text{O}$ , with the zinc salt,  $\text{ZnHAsO}_4\cdot\text{H}_2\text{O}$ ; sodium cupric uranyl acetate,  $\text{NaCu}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9\cdot 9\text{H}_2\text{O}$ , with the corresponding magnesium (see page 5), manganous, ferrous, nickel, cobaltous, and zinc salts; further, also, the formates, malates, benzenesulphonates, etc., of these same metals. Finally, bivalent vanadium appears in certain compounds isomorphously replacing the above metals; namely, in the heptahydrated sulphates and in the double sulphates of the  $\text{K}_2\text{Mg}(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$  type.

A further group of elements which regularly replace one another isomorphously is that of the metals calcium, strontium, barium, and lead. The oxides, the hydrated chlorides, and the azides of calcium, strontium, and barium crystallise respectively alike; in addition to these, the lead salt is also isomorphous in the case of the nitrates, bromates, carbonates, sulphates, etc., and there are isomorphous salts of these metals known, derived from many organic acids. In many cases the calcium salt appears different from the others (the propionate, for example, which even forms double compounds with the propionates of strontium, barium, and lead), also the tartrate and malate. Even when the calcium salt is isomorphous with the others, its angles as a rule exhibit greater differences from those of the isomorphous salts than these do among themselves. The somewhat exceptional position of the first member of this series of metals further appears from the fact that the calcium salt can also functionate as a replacer of the previously mentioned series of metals which begins with magnesium. The salts of these two series of metals are in general not isomorphous, and in many cases they crystallise with unequal amounts of water of crystallisation, which of itself excludes all comparison. In some cases, however, the isomorphous replacement of calcium and magnesium by each other cannot be doubted, as in the carbonates (calcite and magnesite); but these form in addition a double compound (dolomite), containing equal atomic proportions of calcium and magnesium; this, though it possesses similar form, is of lower symmetry. A similar state of affairs exists with the silicates, as shown by the minerals diopside,  $\text{CaMg}(\text{SiO}_3)_2$ , and forsterite,  $\text{CaMgSiO}_4$ ; in these the magnesium can be replaced by other metals of the same series, such as manganese, iron, etc. Still rarer than these are the cases in which strontium and barium can replace a metal of the magnesium series; above  $700^\circ$  strontium carbonate is isomorphous with calcium car-

bonate, and therefore with magnesite; and barium tungstate,  $2\text{BaW}_4\text{O}_{13} \cdot 19\text{H}_2\text{O}$ , is isomorphous with the corresponding cobalt salt,  $2\text{CoW}_4\text{O}_{13} \cdot 19\text{H}_2\text{O}$ . On the other hand, the difference between the two series appears very distinctly in the non-existence of a cubic calcium spinel, whilst for all bivalent metals of the magnesium series the spinels supply an exceptionally good example of their isomorphous replaceability; further examples are: the arsenates of the  $\text{MgHAsO}_4 \cdot \text{H}_2\text{O}$  type; the formates, which differ from those of the calcium series even in the amount of water of crystallisation, and which also form double salts with lead formate; the acetates, malonates, and other salts.

In the periodic system of the elements the metals of the platinum group stand in close relation to those of the iron group, and, in accordance therewith, the members of both are capable of isomorphously replacing one another, as is shown by the complete agreement of sperrylite,  $\text{PtAs}_2$ , and laurite,  $\text{RuS}_2$ , with the corresponding iron-group compounds which constitute the pyrites group of minerals, and also by the perfect isomorphism of potassium palladiocyanide,  $\text{K}_2\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ , with the nickelocyanide,  $\text{K}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ . Tin, through the analogy of certain compounds, associates itself with the platinum metals, so that isomorphous relationships with stannous compounds were to be expected, as between these and the compounds of bivalent lead, mercury, and copper. Apart from similarities in the crystallographical relationships of stannous chloride,  $\text{SnCl}_2$ , and lead chloride,  $\text{PbCl}_2$ ; of mercuric oxide,  $\text{HgO}$ , and lead oxide,  $\text{PbO}$ ; of cupric sulphide,  $\text{CuS}$ , and mercuric sulphide,  $\text{HgS}$ , it is found that the potassium double chlorides,  $\text{K}_2\text{SnCl}_4$  and  $\text{K}_2\text{HgCl}_4$ , as also the ammonium salts,  $(\text{NH}_4)_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HgCl}_4 \cdot 2\text{H}_2\text{O}$ , exhibit such closely agreeing forms that they must be assumed to be really isomorphous. Further, copper and mercury replace each other in the isomorphous compounds of types  $(\text{N}(\text{CH}_3)_4)_2\text{RCl}_4$  and  $(\text{N}(\text{C}_2\text{H}_5)_4)_2\text{RCl}_4$ , and in the compounds of quinoline hydrochloride with cupric and mercuric chlorides, described by Borsbach.

**III. Group of the trivalent elements.**—The relations of the first member of this group (boron) to those elements which follow it, are limited to the similarity which the monoclinic crystals of hydrargyllite,  $\text{Al}(\text{OH})_3$ , exhibit with the triclinic crystals of sassoline,  $\text{B}(\text{OH})_3$ , and to the analogy of the rôle played by boron and aluminium in some complicated silicates. On the other hand, aluminium is quite generally replaced by trivalent chromium,

manganese, and iron, and, not infrequently, also by titanium. Examples are supplied by the oxides,  $\text{Al}_2\text{O}_3$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ; the hydroxides,  $\text{AlO.OH}$ ,  $\text{MnO.OH}$ ,  $\text{FeO.OH}$ ; the various aluminium and ferric sulphates, silicates (here titanium also, *e.g.*, in the garnet group), etc.; also the salts in which the metallic oxides represent the acidic constituent, as in the spinels,  $\text{Mg}(\text{AlO}_2)_2$ ,  $\text{Mg}(\text{CrO}_2)_2$ ,  $\text{Mg}(\text{MnO}_2)_2$ ,  $\text{Mg}(\text{FeO}_2)_2$ . The isomorphous replacement of the most widely varying trivalent metals has been shown with great completeness in the group of the alums, which are, it is true, fairly complex compounds; in these the aluminium of common alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , may be replaced by any of the following:—vanadium, chromium, manganese, iron, cobalt, gallium, rhodium, indium, thallium(?), titanium. There is probably also isomorphism between compounds of trivalent indium and thallium in the case of certain double chlorides.

The trivalent metals of the so-called rare earths replace one another isomorphously in the hydrated sulphates, which have been very completely investigated, but isomorphism between the salts of these metals and the corresponding salts of iron or aluminium, has been proved only in the case of some complicated silicates, such as orthite. Isomorphism is also assumed to exist between certain complex double nitrates of the rare-earth metals and those of bismuth, but this has not yet been sufficiently proved by a comprehensive crystallographic investigation.

Amongst the platinum metals, two (rhodium and iridium) appear as trivalent in a series of compounds, and here again cases of isomorphism occur, for example,—the complex cyanides,  $\text{K}_3\text{Ir}(\text{CN})_6$  and  $\text{K}_3\text{Rh}(\text{CN})_6$ , with  $\text{K}_3\text{Cr}(\text{CN})_6$ ,  $\text{K}_3\text{Mn}(\text{CN})_6$ ,  $\text{K}_3\text{Co}(\text{CN})_6$ , and  $\text{K}_3\text{Fe}(\text{CN})_6$ ; the ammonia addition compounds,  $\text{Ir}(\text{NO}_3)_3 \cdot 6\text{NH}_3$  with  $\text{Co}(\text{NO}_3)_3 \cdot 6\text{NH}_3$ , and  $\text{Cl}_2\text{Rh}_2(\text{NH}_3)_{10}\text{Cl}_4$  with  $\text{Cl}_2\text{Co}_2(\text{NH}_3)_{10}\text{Cl}_4$  (chloropurpureo-cobaltichloride).

IV. Group of the quadrivalent elements.—The profound differences which the first and second members of this group (carbon and silicon) exhibit from the chemical point of view, are reflected in the fact that, except for the agreement between the cubic crystalline forms of the two iodides,  $\text{Cl}_4$  and  $\text{SiI}_4$ , there is no isomorphism between analogously constituted compounds of the two elements—between the carbonates and the silicates, for example—and also in the fact that the two elements unite to form a very stable compound,  $\text{CSi}$  (carborundum), whose crystalline form exhibits no relation to that of either of its elements.

On the other hand, silicon can be isomorphously replaced by titanium and by tin. Although the form of silica corresponding to the isomorphous dioxides rutile,  $\text{TiO}_2$ , and cassiterite,  $\text{SnO}_2$ , is unknown (as is also that of zirconia,  $\text{ZrO}_2$ ); and, further, the agreement between the crystalline forms of the iodides  $\text{SiI}_4$ ,  $\text{TiI}_4$ ,  $\text{SnI}_4$ , and between the compounds of phosphoric anhydride with the dioxides of silicon, titanium, zirconium, and tin, is in each case discounted to a certain extent by reason of these substances all belonging to the cubic system, the isomorphous replacement of these elements appears indubitably in a series of fluo-salts, such as those of the types  $\text{SrSiF}_6 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ , etc. In the isomorphous group of chloro-salts corresponding to the last-mentioned type of fluo-salt, platinum also appears replacing tin isomorphously; the anhydrous salts,  $\text{K}_2\text{SnCl}_6$  and  $\text{K}_2\text{PtCl}_6$  (as also  $\text{K}_2\text{PdCl}_6$ , etc.), are also isomorphous; so also are the chloroplatinates and chlorostannates of a great variety of alkyl-ammonium radicals. Further, the chloro-salts  $\text{K}_2\text{TeCl}_6$ ,  $\text{Cs}_2\text{PbCl}_6$  and  $\text{Cs}_2\text{SbCl}_6$  crystallise in the octahedral form which is characteristic of the similarly-constituted salts  $\text{K}_2\text{SnCl}_6$  and  $\text{Cs}_2\text{PtCl}_6$ . The relation here observed between quadrivalent lead and tin occurs again in the isomorphism of the acid fluo-salts  $\text{K}_3\text{HSnF}_8$  and  $\text{K}_3\text{HPbF}_8$ . Finally, quadrivalent cerium appears to be isomorphous with thorium in the nitrates  $\text{MgR}^{\text{IV}}(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$ , and the latter element with uranium in the sulphates  $\text{Th}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{U}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ .

V. The nitrogen group (trivalent and quinquivalent elements).—As is to be expected from the chemical characters, isomorphous relationships are in general not observed between nitrogen and the succeeding elements of this group. Thus, even the tetra-alkyl-phosphonium bromides and iodides crystallise differently from the corresponding ammonium derivatives; and, similarly, triphenylamine,  $\text{N}(\text{C}_6\text{H}_5)_3$ , notwithstanding the size of its molecule, differs from the corresponding substances  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{As}(\text{C}_6\text{H}_5)_3$ ,  $\text{Sb}(\text{C}_6\text{H}_5)_3$ , and  $\text{Bi}(\text{C}_6\text{H}_5)_3$ . On the other hand, the chloroplatinates of tetraethylammonium, tetraethylphosphonium, and tetraethylarsonium (all cubic, however) may possibly be considered as isomorphous.

With phosphorus there begins a series of elements which replace one another isomorphously in the most diverse classes of compounds, and which even can assume similar crystal forms in the free state; these are phosphorus, arsenic, antimony, and

bismuth. Amongst those compounds in which these elements have a trivalent character there is regularly isomorphous replacement—in the oxides, sulphides, iodides, and especially in numerous natural thio-salts (the thiarsenites, thiantimonites, and thio-bismuthites). As quinquivalent elements, phosphorus, vanadium, and arsenic replace one another in the apatite— $\text{Ca}_5\text{Cl}(\text{PO}_4)_3$ —group, and in numerous isomorphous groups of hydrated phosphates and arsenates (the corresponding vanadates have been less fully investigated crystallographically); the compounds  $\text{P}(\text{C}_2\text{H}_5)_3(\text{C}_2\text{H}_4\text{Br})\text{Br}$  and  $\text{As}(\text{C}_2\text{H}_5)_3(\text{C}_2\text{H}_4\text{Br})\text{Br}$ , which crystallise cubic, can also be looked upon as isomorphous.

Whilst niobium and tantalum replace one another isomorphously in all known cases (fluo-compounds, tantalates and niobates) the question of the isomorphism of the oxides  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  with  $\text{V}_2\text{O}_5$  requires further investigation.

**VI. Oxygen group (bivalent, quadrivalent, and sexivalent elements).**—A true isomorphous replacement of oxygen by the succeeding members of the group does not exist, and even very complicated sulphur compounds are not isomorphous with the corresponding oxygen compounds; thus, the thiosulphates crystallise differently from the sulphates, and not only carbamide (urea) and thiocarbamide, but also their phenyl derivatives—even diphenylcarbamide and thiocarbanilide, notwithstanding the size of their molecules—are different. On the other hand, there is unmistakably a certain analogy in the cubic structure of certain exceedingly simple compounds of the two elements, as between cuprous oxide and sulphide, magnesium oxide and sulphide, zinc oxide and sulphide (in this case there is also agreement in the symmetry for a second—a hexagonal—modification); also between the oxides and sulphides of calcium, strontium, and barium; and, finally, between the spinels and certain analogous thio-salts (linnéite,  $\text{Ni}_3\text{S}_4$ ). The agreement between certain metallic tellurides, which crystallise cubic, and the corresponding sulphides and selenides, must, in the same way, be looked upon as constituting no true isomorphism; the other compounds of tellurium do not agree crystallographically with the compounds of sulphur and of selenium.

In this group the most important series, as regards isomorphous replacement, are formed by the elements sulphur, chromium, and selenium, when these have a sexivalent character. The rhombic potassium salts,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{CrO}_4$ , and  $\text{K}_2\text{SeO}_4$ , have been mentioned

already (page 69), and with these are also to be ranged  $K_2MnO_4$  and  $K_2FeO_4$ , possibly also  $K_2MoO_4$  and  $K_2WO_4$ ; these two have not yet been prepared in suitable crystals (the thio-salts corresponding to them exhibit a certain analogy of crystalline form with the preceding salts). Ammonium chromate and molybdate are isomorphous with the monoclinic form of the selenate, and isomorphism has also been established between ammonium magnesium sulphate,  $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ , and the corresponding molybdate,  $(NH_4)_2Mg(MoO_4)_2 \cdot 6H_2O$ , and also between the three magnesium salts,  $MgSO_4 \cdot 5H_2O$ ,  $MgCrO_4 \cdot 5H_2O$ , and  $MgMoO_4 \cdot 5H_2O$ . In addition to the quite general isomorphism between analogous sulphates and selenates, isomorphism is also observed not only with the chromates and the molybdates, but also with the tungstates, in salts of the type  $Na_3Li(SO_4)_3 \cdot 6H_2O$  and those of the type of Glauber's salt,  $Na_2SO_4 \cdot 10H_2O$ . Isomorphism is also regularly observed in analogously constituted molybdenum and tungsten compounds, such as the normal molybdates and tungstates of calcium, strontium, barium, and lead; the compounds  $(NH_4)_2MoO_2F_4$  and  $(NH_4)_2WO_2F_4$ , and other similar salts.

**VII. The fluorine group.**—It has been already mentioned on page 71, that, as regards isomorphism, fluorine appears less closely related to the other halogens than these are among themselves. As a matter of fact, the fluorides  $KF$  and  $NH_4F$  crystallise differently from the chlorides  $KCl$  and  $NH_4Cl$ , and  $SnF_2$  differently from  $SnCl_2$ ; and the agreement in the crystalline forms of the sodium salts,  $NaF$  and  $NaCl$ , is not decisive, because here we have to deal with cubic substances. An actual isomorphism between corresponding compounds of fluorine and chlorine becomes recognisable only when the compounds are of a complex nature, such as the magnesium halogeno-stannates,  $MgSnF_6 \cdot 6H_2O$  and  $MgSnCl_6 \cdot 6H_2O$ ; the apatites,  $Ca_3F(PO_4)_3$  and  $Ca_3Cl(PO_4)_3$ ; the fluo- and chloro-naphthalenesulphonic chlorides, and the ethyl esters derived from them.

On the other hand, as mentioned on page 70, chlorine, bromine, and iodine replace one another isomorphously in all compounds; the exceptions to this generalisation are only apparent, and are due to the fact that the compound containing iodine (or bromine and iodine) forms the corresponding modification only at a higher temperature. A well-known example of this is provided by the group of the silver halides,  $AgCl$ ,  $AgBr$ , and  $AgI$ : the first and



second crystallise cubic; the last crystallises at ordinary temperatures in a hexagonal form, its cubic modification, isomorphous with the others, being stable only at higher temperatures. Ammonium bromide is isomorphous with ammonium chloride, but ammonium iodide is not; although it also crystallises cubic, the modification is one which corresponds to that of the three halides of potassium, which are completely isomorphous; the corresponding modification of ammonium chloride is produced only at higher temperatures. The exceptional character of the iodine compound, due to polymorphism, appears also in the iodides of the bivalent metals, such as mercury, and those of the trivalent metals, such as antimony; whilst in the case of the double halides all three compounds, as a rule, belong to the corresponding modification at the ordinary temperature; the same is the case with still more complex compounds, as in the apatites, where the fluorine, chlorine, bromine, and iodine compounds are completely isomorphous. On the other hand, only sodium bromate,  $\text{NaBrO}_3$ , agrees with the chlorate,  $\text{NaClO}_3$ —the iodate,  $\text{NaIO}_3$ , crystallising differently. The corresponding potassium salts are all different from one another, and it is evident that in this group very complicated polymerism obtains. As regards a chlorine compound and the corresponding bromine compound, however, in by far the great majority of cases the limits of stability for other possible modifications are such that at ordinary temperatures the two substances are obtained in corresponding states, and these two substances are then completely isomorphous—as a rule with very close agreement in the angles; somewhat greater angle differences manifest themselves only in cases where the equivalent volumes of the two substances are appreciably different from each other, as with *p*-dichlorobenzene and *p*-dibromobenzene.

Although there are, amongst the examples collected in the preceding paragraphs, some whose isomorphous relationships would require to be subjected to a more thorough investigation, it is nevertheless amply evident, from the well-established facts, that the atoms of two closely related elements possessing the same valency are capable of replacing each other without the crystal structure thereby undergoing any extensive change. The same holds also for the replacement of the potassium atom by the ammonium radical,  $\text{NH}_4$ , in accordance with the complete chemical

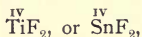
analogy between ammonium and the univalent alkali metals.

The cyanogen radical, CN, in its chemical relations behaves very like a halogen, and it is, therefore, natural to expect the isomorphous replaceability of cyanogen and the halogens. If, however, the existing observations are examined, then (apart from the salts of the alkali metals, whose mere similarity of form is no criterion, since they belong to the cubic system) it is found that there is in general no similarity of crystallographic character; in most cases, also, the cyanogen compounds which in composition correspond to the complex halides, either do not exist, or, if they do (as in the case of potassium ferricyanide and the analogous chloro-salts and fluo-salts), the question of their isomorphism has not been investigated.

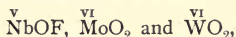
On the other hand, a not inconsiderable number of cases have been established, in which two compounds, differing from one another by the replacement of an atom by an atomic group of similar valency, exhibit such thorough agreement in crystallographical character that they have been designated as isomorphous substances. Such relationships are exhibited, for example, by certain minerals containing hydroxyl and fluorine (wagnerite group, topaz), and these have given rise to the assumption of an isomorphous replacement of fluorine and hydroxyl. (An attempt by Fels, to discover isomorphism between chlorine derivatives and hydroxyl derivatives of benzene, was without result, probably owing to the fact already mentioned, that, as regards isomorphism, the chlorine compounds diverge considerably from the corresponding fluorides.) Of organic fluorine compounds suitable for comparison, only a few have been closely investigated, but, as a matter of fact, one case described by Gossner likewise shows such close relationships between the respective substances, as to justify the conclusion that, in substances of complex composition, an isomorphous replacement of hydroxyl and fluorine can really take place. In the same

way it is possible that in the minerals related to sodalite the replacement of chlorine by other salt radicals is to be explained by the size of the molecule. On the other hand, it is scarcely possible to include, under the heading of isomorphism in the stricter sense, the striking resemblances in crystalline form which, according to Hiortdahl's observations, the salts of the univalent radicals  $\text{Sn}(\text{CH}_3)_3$ ,  $\text{Sn}(\text{C}_2\text{H}_5)_3$ , etc., exhibit with the corresponding salts of the univalent metals (as do also the analogous salts of the bivalent radicals,  $\text{SnR}_2$ , with those of bivalent metals); these relationships, however, merit further investigation.

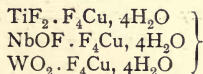
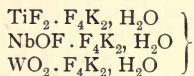
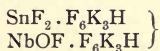
The researches of Marignac have resulted in the recognition of the complete analogy in crystalline character of the members of several different series of salts, where the various members of any one series differ among themselves, as regards chemical character, in having the bivalent group

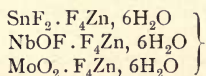


replaced by the groups (likewise bivalent)



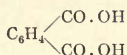
which must, therefore, be looked upon as replacing one another isomorphously. In the following table several series of this kind are expressed by formulæ which are so written that the groups above mentioned appear separated from the other constituents :



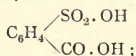


Though the constitution of the substances here dealt with can by no means be considered as clearly established, there is, on the other hand, an unmistakable agreement of crystal form in the case of organic compounds of well-established constitution, which likewise differ from one another by the mutual replacement of radicals of like valency but dissimilar constitution. A number of such cases are given here.

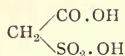
The carboxyl group,  $\text{—CO.OH}$ , and the sulphonyl group,  $\text{—SO}_2\text{.OH}$ , possess a similar chemical character. As Zirngiebl has shown,<sup>1</sup> there is a great similarity in the crystallographical relationships of the analogous salts of phthalic acid,



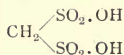
and of *o*-sulphobenzoic acid,



notwithstanding the relatively great difference between the equivalent volumes, this similarity extends even to the values of the topic parameters. There is, further, a similar relation between benzoic acid,  $\text{C}_6\text{H}_5\text{.CO.OH}$ , and benzene sulphonic acid,  $\text{C}_6\text{H}_5\text{.SO}_2\text{.OH}$ ; and, finally, between sulphoacetic acid,



and methionic acid,



The alkali metal salts of imido-sulphonic acid are crystallographically very closely similar to those of methionic acid; the former acid differs from the other in having the  $\text{CH}_2$  group re-

<sup>1</sup> *Zeits. f. Kryst.* 1902, 36, 117 *et seq.*

placed by the imido-group, NH, which in many respects exhibits a chemical behaviour similar to that of the former.

There are very striking similarities in the crystalline forms of some substances whose constitution differs as regards the nature of the linking between certain carbon atoms, the group  $\text{H}_2\text{C}-\text{CH}_2$ , being replaced by  $\text{HC}=\text{CH}$ ., or by  $\text{C}\equiv\text{C}$ ., as in the anhydrides of succinic acid and malic acid, with which also even that of itaconic acid is to be associated. (In this group the comparison with the imides would also be of interest, *i.e.*, the determination of the alteration produced by the replacement of oxygen by the imido-group.) Still more thoroughly known is the following series of substances, which exhibit a striking agreement in their crystallographical characters :—



Acenaphthene and acenaphthylene are similarly related. In this connection also fall to be considered the similarities of crystal form exhibited by quinone and *p*-diketohexamethylene ; by phthalic acid and its hydro-derivatives ; and, finally, by the salts, esters, and bromides of the hydrogenated terephthalic acids.

Whether or not, in the preceding and similar cases, the relationships between the respective substances are identical with those which are exhibited by two typically isomorphous salts, such as potassium sulphate and rubidium sulphate, can only be made out by further investigation. On the other hand, there is good reason to class under the head of isomorphism those cases in which, within a large chemical molecule, two atoms of a univalent metal are replaced by a single atom of a bivalent metal without any considerable change of crystal structure, or those in which two atoms of a bivalent metal are replaced by one of a trivalent and one of a univalent metal. Such replacements are often observed—as, for example, that of Ca and  $\text{Na}_2$  in different silicates, especially those which are hydrated ; of  $\text{Cu}_2$  (cuprous) and Pb in many natural thio-salts ; of  $\text{Ca}_2$  and AlLi or FeNa in the pyroxene group of minerals ; and, finally, of SiNa and AlCa in the series of the felspars. In the latter case

the two compounds (albite,  $\text{NaAlSi}_3\text{O}_8$ , and anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) behave in all respects like isomorphous substances, in the closest sense of the word, and, in addition, possess almost identical equivalent volumes.

As appears from the introductory considerations at the beginning of this section, the isomorphism of two substances depends on the fact that the entrance of the atoms, or (to take into account the last-mentioned relationships) groups of atoms, which replace each other in the substances, produces a similar change in the crystal structure of the compound from which they are in common derived. Since the extent of this change depends not only on the nature of the substituting atoms or groups of atoms, but also on that of the original substance, it follows that the differences which are to be observed in cases of isomorphous replacement by the same substituents, are different in different isomorphous series; and in general they must be smaller the greater the number of atoms common to the isomorphous substances. There cannot exist, therefore, any sharp boundary between isomorphous substances, in the narrowest sense, and others which exhibit morphotropic relationships to one another; this is the reason why the idea of isomorphism cannot be strictly defined, and attempts have been made to discover other properties, over and above the analogy of chemical constitution and the close agreement of the crystal structure, which would allow of isomorphous substances in the strictest sense of the word being distinguished from those less closely related to one another. In this connection the behaviour of isomorphous substances towards their solutions comes especially into consideration.

### B. Relations between Crystals and Solutions of Isomorphous Substances

**Episomorphism.**—When a crystal of one substance is introduced into the solution of another substance which is isomorphous with it, then, if the first substance is also soluble in the solution, there will, of course, be partial



dissolution ; should, however, in consequence of evaporation, a separation of the substance originally present in the solution take place, then the crystal will grow by the parallel accretion of particles of the substance, just as it would grow in its own solution. Thus, an octahedron of chrome alum grows in a solution of aluminium alum, and *vice versâ*. In the latter case, should the crystal also possess cubic faces, then a much larger proportion of chrome alum will be deposited upon them in a given time than upon the octahedral faces ; this can be easily observed, owing to the dark colour of the chromium salt. Very fine parallel overgrowths (*episomorphs*) formed in this way from salts possessing different colours, were prepared by K. von Hauer ; as, for example, those of magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , on magnesium chromate,  $\text{MgCrO}_4 \cdot 7\text{H}_2\text{O}$ , or on nickel sulphate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  ; of potassium magnesium sulphate,  $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , on the corresponding cobaltous and nickel salts,  $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . In nature, episomorphs of potash and soda felspars are very common.

The behaviour of a supersaturated solution when it is inoculated with a crystal of some substance with which the solute is isomorphous, is closely allied to the phenomenon just considered. It is well known that the supersaturated solution of a salt can be made to crystallise immediately by contact with a particle of the solid salt. The same result is attained, however, by contact with a crystal of some substance which is isomorphous with the salt in solution, as has been proved by experiments on the sulphates mentioned above, by various observers.

Under certain circumstances each of these phenomena can be employed as a means of recognising isomorphism in two substances, but it must be noted that there are cases of the regular growth of crystals of non-isomorphous substances, closely allied in character to episomorphs ; and further, that the crystallisation of supersaturated solutions can also be induced by foreign substances. These phenomena,

therefore, serve rather as confirmatory evidence of the existence of isomorphism and not as independent proofs of it; such proof must, in the first instance, be based on the recognition of a close agreement in crystal structure, as brought to light by the similarity as regards cohesion, the values of the angles, the phenomena associated with the growth and dissolution of the crystals, as also by the close agreement in the values of the topic parameters. Intimately connected with the latter, *i.e.*, with the close similarity as regards distribution in space, is that peculiarity which forms the most characteristic property of isomorphous substances—the ability, namely, to mix with one another in varying proportions to form homogeneous crystals.

### C. Isomorphous Mixtures

When a solution containing two or more isomorphous substances, mixed in any proportions, is allowed to crystallise, there are formed in it crystals which likewise contain the isomorphous substances in intimate mixture. If the quantity of crystallised substance deposited is small in proportion to the quantity of solution, so that the separation produces no appreciable variation in the composition of the solution, then the crystals are homogeneous, possessing the same composition throughout. This composition, like that of the solution, does not necessarily correspond to any definite molecular proportions of the substances present. In this respect isomorphous mixtures differ from the so-called **molecular compounds**.

The assumption has been made by van 't Hoff,<sup>1</sup> that an isomorphous mixture of two substances, A and B, is a **solid solution** of A in B, just as the liquid from which the crystals separate can be looked upon as a solution of A in the solution of B, and he further assumes that the gas laws apply to the solid solution just as they do to the liquid one. If such be the case, then equilibrium between the solution and the mixed crystals exists only when the composition of

<sup>1</sup> *Zeits. f. phys. Chem.* 1890, 5, 322; *Journ. C. S.* 58, 1044.

the mixed crystals, expressed in molecular percentage of A, bears a certain ratio to the composition of the solution, similarly expressed; this ratio being given by the so-called law of distribution. With certain provisos, therefore, it would be possible, from the constancy or variability of this ratio, to draw conclusions regarding the molecular nature of the substance A in the mixed crystals; and, since for isomorphous substances a similar molecular condition is to be assumed, the same conclusions apply to B. Most of the experimental investigations regarding this subject, carried out by Roozeboom, Muthmann, Fock, etc., have led to the conclusion that the salts examined are present in the mixed crystals as simple molecules.

Even although this method, as has been shown more especially by Bodländer,<sup>1</sup> is not capable of yielding any unimpeachable determination of the molecular complexity of solid substances, the above result is nevertheless in agreement with those views regarding isomorphous mixtures which, on the basis of the theory of crystal structure, we are forced to adopt. In the production of isomorphous mixtures it is evidently necessary that the molecules of the individual substances present in the solution should be similarly available for the formation of the crystals forming in it. Taking into account the consideration brought forward on page 13 (according to which the idea of molecular weight has no longer any definite significance for substances in the crystallised condition), this may also be expressed as follows:—The regular point systems which determine the arrangements of the atoms in the crystal structure remain in equilibrium, even should the places of a proportion of the atoms be taken by atoms of the kind which replace them isomorphously. This equilibrium will evidently be characterised by a more complete stability the less the forces which determine the crystal structure differ for the isomorphous substances present in the mixture, *i.e.*, the smaller the differences in the dimensions

<sup>1</sup> N, *Jahrb. f. Min, Geol.*, etc., 1898, Beil.-Bd., 12, 52,

of their structure units, as expressed by the topic parameters. Further, the mixed crystal will appear more completely homogeneous the greater the regularity in the distribution of the atoms which replace one another isomorphously; and it will exhibit properties which, as a rule, stand between those of the two substances crystallising together. In the case of an unbroken series of mixtures of two isomorphous substances, there will therefore occur a continuous transition of the properties from those of the one substance to those of the other.<sup>1</sup>

According to this view each component of an isomorphous mixture would retain its own specific volume, so that the volume of the mixture would correspond to the sum of the volumes of the components. That this is in fact the case has been shown by Tschermak for the mixtures of albite and anorthite, and by Pettersson for those of certain sulphates and selenates. This subject was made the subject of very thorough investigation by Retgers,<sup>2</sup> and for this purpose he specially developed the method of density determination by means of dense liquids (page 44), by which it is possible to carry out the determination with great accuracy on quite small crystals, which are more easily obtained in a homogeneous condition.

If  $d$  and  $d'$  represent the densities of two isomorphous substances,  $a$ , the volume percentage of the second substance which is present in the mixture, and  $D$  the density of the mixed crystals, then the latter is determined by the expression

$$D = d + a(d' - d) / 100,$$

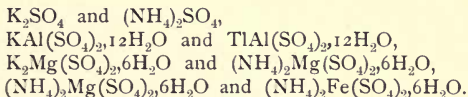
*i.e.*, in an isomorphous mixture the variation of density with

<sup>1</sup> Retgers made this behaviour the basis of the following definition of isomorphism: "Two substances are really isomorphous only when the physical properties of their mixed crystals are continuous functions of their chemical composition."

<sup>2</sup> *Zeits. f. phys. Chem.* 1889, 3, 497; 4, 593; 1890, 5, 436; 6, 193; 1891, 8, 6; *Journ. C. S.* 56, 931; 58, 328, 1208; 60, 146, 1151,

composition (the latter being expressed in percentage by volume) is represented by a straight line.

To test the correctness of this relation, Retgers investigated the following pairs of salts, whose members differ sufficiently in density, and form isomorphous mixtures in all proportions :



In all of these cases it was observed throughout that, within the limits of experimental error, the proportionality between the density and the composition of the mixtures was that required by the preceding equation.

The salts employed for the above investigations are such as can form mixtures in all proportions, and this of course can be the case only when dealing with substances which display complete isomorphism, *i.e.*, with substances which exhibit only slight differences of crystal structure, not merely as regards relative dimensions but also as regards the absolute values, which involves closely agreeing equivalent volumes. A further condition is that the behaviour of the respective substances as regards solubility should not differ too widely.

In the case of two substances which can crystallise in several polymorphous modifications, the existence of a continuous series of isomorphous mixtures of the substances, entirely free from gaps, is possible only if the stability of the corresponding state in which the substances crystallise together should not be widely different in the two cases. If, on the contrary, the temperature intervals for the stability of the individual modifications of the two substances differ so widely that, under the conditions ruling during the crystallisation, the corresponding state of the one substance is metastable, then as a rule this substance can crystallise along with the other in the form which is stable

for it, but only to a limited extent. Within this limited range, however, the two substances form mixtures to which the same general rules apply as for complete mixture series; and this circumstance serves as an excellent means of establishing the dimorphism (or isodimorphism) of a group of substances possessing analogous composition.

Such cases also were first quantitatively investigated by Retgers. The two salts, ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , at first appear to contradict the rule stated on page 74, that in analogous compounds magnesium and iron (ferrous) can always replace each other isomorphously; for the

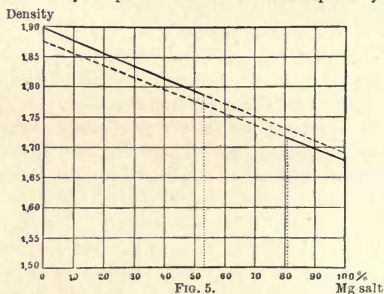


FIG. 5.

crystals of the first-mentioned salt are monoclinic prismatic, whilst those of the other are rhombic bisphenoidal. From aqueous solutions, at ordinary temperature, it is possible to obtain mixed crystals containing up to 54 per cent. of magnesium sulphate and possessing the monoclinic form of ferrous sulphate. There must, therefore, be a second (a monoclinic) form of magnesium sulphate, which can form isomorphous mixtures with ferrous sulphate. There is a gap between the mixture containing 54 per cent. and the next higher one, which contains 81 per cent. of the magnesium salt, intermediate mixtures being unknown; mixtures from this point up to pure magnesium sulphate exist, and they exhibit the rhombic form of the latter salt. If the densities of these various mixtures are plotted against the corresponding percentage compositions, as in Fig. 5, it is seen that the values lie upon two separate and distinct straight lines, not parallel to each other. By prolongation of the upper line, the density of the assumed mono-



clinic modification of magnesium sulphate is found to be 1.691, or 0.014 higher than that of the rhombic modification, whilst similarly the rhombic modification of ferrous sulphate would appear to have a density of 1.875, or 0.023 lower than that of the monoclinic modification; in both cases, therefore, the monoclinic modification is the denser of the two. The fact that mixtures containing more magnesium sulphate than ferrous sulphate can still form monoclinic crystals, indicates that the limit of stability for this form of magnesium sulphate can not be very far removed from the ordinary temperature. As a matter of fact, Marignac obtained, from supersaturated solutions in the cold, magnesium sulphate crystals which immediately underwent transformation when they were removed from the solution, and which, therefore, consisted of a modification unstable at ordinary temperature. When measured approximately, these crystals gave angle values which agree very closely with those of ferrous sulphate (Marignac assumed the crystals to be trigonal because they exhibit a rhombohedral habit, which ferrous sulphate itself does). A rhombic form of ferrous sulphate has not as yet been prepared; this was to be expected, since the salt crystallises in the rhombic form only in mixtures possessing a marked preponderance of magnesium sulphate. This case, therefore, is undoubtedly one of isodimorphism, and the apparent exception to the rule of the isomorphous replacement of magnesium by ferrous iron is completely explained.

Sodium nitrate is trigonal, and silver nitrate rhombic, but Retgers prepared mixtures which had the form of the sodium salt, and contained up to 52.5 per cent. of silver nitrate; from the densities of these he calculated the value for the trigonal modification of silver nitrate present in them to be 4.19, whilst the rhombic modification has a density of 4.35. On the other hand, sodium nitrate crystallises rhombically only in mixtures which contain a great excess of silver nitrate. In agreement herewith, no rhombic modification of pure sodium nitrate has as yet been obtained, whilst the second modification (trigonal) of the silver salt is formed when the fused substance is allowed to cool, even though no sodium nitrate is present (Lehmann).

As has been shown by the investigations of Gossner,<sup>1</sup> particularly well-marked examples of limited miscibility are provided by potassium and ammonium salts, whose dimorphism can in this way be shown even in cases of apparently complete agreement

<sup>1</sup> *Zeits. f. Kryst.* 1903, 38, 110 et seq.

of crystalline form. Thus, potassium chloride and ammonium chloride (as also potassium bromide and ammonium bromide), which are cubic, and even crystallise in the same symmetry class, form mixtures only to a very limited extent; on the one hand crystals are obtained, possessing the habit of the potassium salt, which contain only quite small proportions of ammonium chloride; and, on the other, crystals with the habit of the ammonium salt, which contain only quite small proportions of potassium chloride. The explanation of this fact is that there exists a second modification of ammonium chloride, likewise cubic, which, however, is extremely labile, and therefore forms isomorphous mixtures with the ordinary modification of potassium chloride (which is isomorphous with this modification of ammonium chloride, and not with the ordinary one) only when there is a great excess of the potassium salt. Similar behaviour is exhibited by the nitrates of potassium and ammonium, both of which crystallise rhombic, but in forms which cannot without straining be referred to each other, and which in fact do not correspond to each other. From mixed solutions two kinds of crystals separate, the one having the form of potassium nitrate and containing little ammonium nitrate, the other having the form of ammonium nitrate and, though containing larger proportions of the potassium salt, nevertheless consisting chiefly of ammonium nitrate; there is therefore a considerable gap in the series of mixtures.

Cases similar to the preceding examples are not uncommon, in which two analogously constituted compounds, which might be expected to exhibit isomorphism, exhibit certain similarities in crystalline form, and were therefore formerly designated as isomorphous. This was done even when the reference to a common fundamental form necessitated the multiplication of the parameters by  $\frac{1}{2}$ ,  $\frac{2}{3}$ ,  $\frac{3}{4}$ , or similar factors, so that the faces observed on the crystals became highly improbable, to judge from their symbols. If two such substances are examined as regards their miscibility, it is regularly found that the one is able to take up only very limited quantities of the other in isomorphous admixture, so that the two crystalline substances—we shall designate them as  $A_1$  and  $B_2$ —regarded as isomorphous do not represent corresponding states; the

substance A possesses a second modification,  $A_2$ , which is really isomorphous with  $B_2$ , and therefore forms mixtures with it, whilst those mixtures in which  $A_1$  preponderates contain the substance B in a second form,  $B_1$ , isomorphous with  $A_1$ . The similarity between the crystalline forms of  $A_1$  and  $B_2$  depends on the fact that the two modifications of A (and likewise those of B) present certain resemblances ; as already mentioned on page 34, however, a closer investigation of such cases always shows that, as regards the natural fundamental form, the cohesion, etc., there exist such profound differences that an essentially different crystal structure must be assumed for the two modifications.

From the fact that two substances give rise to only the two extremities of a mixture series, it is therefore safe to conclude that they are isodimorphous. The length of the mixture curve at the one side or the other gives, as the above examples have shown, an indication as to which of the two unknown modifications possesses the greater stability in the pure state, and may therefore be the more easily obtainable.

Sometimes the mixtures of two such **isopolymorphous** substances exhibit, in the middle part of the series, the form of a third modification, in which neither of the individual compounds crystallises when pure.

This was observed by Fock,<sup>1</sup> with the dithionates of potassium and thallium,  $K_2S_2O_6$  and  $Tl_2S_2O_6$ , and by Gossner,<sup>2</sup> with the acid sulphates of potassium and ammonium,  $KHSO_4$  and  $NH_4HSO_4$ . Such phenomena are exceptionally complicated in the case of sulphur and selenium ; ordinary rhombic sulphur can take up to 35 per cent. of selenium in isomorphous mixture, the corresponding modification of selenium being itself unknown ; there is no monoclinic modification of selenium corresponding to the monoclinic sulphur obtained from the fused substance, and isomorphous mixtures do not occur ; the form of a third modification, likewise monoclinic, appears also in mixtures containing from 35 to 66 per cent. of selenium ; another monoclinic form, different from these,

<sup>1</sup> *Zeits. f. Kryst.* 1882, 6, 163.

<sup>2</sup> *Loc. cit.* 1904, 39, 381.

is exhibited by the mixtures containing more selenium, and also by the pure selenium crystallised from solution in hot carbon bisulphide; the form of pure selenium crystallised from carbon bisulphide at ordinary temperature, and that of "metallic" selenium, are unknown on pure sulphur and also on mixtures.<sup>1</sup>

Gaps in an isomorphous mixture series apparently can also arise from the formation of the crystals being disturbed by the separation of other hydrates, or owing to the fact of certain mixtures crystallising less perfectly and therefore being overlooked during the investigation.<sup>2</sup> In such cases the proof that the mixtures belong to a single isomorphous series is supplied by the fact that the two curves, which represent the relation between the density and the composition, for the mixtures actually examined, are not parts of two non-parallel straight lines, as in Fig. 5, page 92, but are parts of one and the same straight line. Complete continuity of the isomorphous mixture series has been proved as yet only for a small number of pairs of salts, and these all exhibit great similarity of the two isomorphous salts, as regards cohesion, greater or less favouring of individual forms during the formation of the crystals, etc., so that a very close agreement of the crystal structures must be assumed. It would therefore be appropriate, in order to avoid arbitrariness in the use of the word "isomorphous," to designate as isomorphous only such substances as possess the property of crystallising together *in all proportions* to form homogeneous mixtures whose properties are continuous functions of their composition. It must be admitted that, in the majority of cases, the proof of isomorphism would require more thorough investigations than at present exist. For example, attempts should be made, by altering the conditions of crystallisation, to complete the separate sections of the incomplete mixture series of isodimorphous substances, as represented in Fig. 5.

The question of the behaviour of two isomorphous sub-

<sup>1</sup> Muthmann, *Zeits. f. Kryst.* 1890, 17, 336.

<sup>2</sup> See Stortenbeker, *Zeits. f. phys. Chem.* 1903, 43, 629; *Journ. C. S.* 84, ii, 470.

stances on separation from a common fused magma is also of importance. In the first place, as regards the solidifying point of such magmas, Küster has found from investigation of a series of pairs of undoubtedly isomorphous substances, that in many cases the solidifying points vary proportionally to the molecular composition of the fused mixture of the two substances, but that in others they deviate not inconsiderably from such proportionality; in his view, the latter condition is brought about by non-homogeneous solidification of the magma. On the other hand, Roozeboom has shown on theoretical grounds that the solidification curve for two isomorphous substances need not necessarily be a straight line, but may equally well be a curve exhibiting a maximum or a minimum, and Reinders has experimentally proved the existence of the latter in the case of fused mixtures of both modifications of mercuric bromide and mercuric iodide. Here the admixture of the higher-melting iodide brings about a lowering of the melting point of the bromide. This is also the case with other substances, which do not stand in isomorphous relationships with one another, and the above-mentioned laws regarding the possible solidification curves of fused mixtures, theoretically deduced by Roozeboom, are applicable both to isomorphous and to non-isomorphous substances. From the form of the fusion curve, therefore, no certain conclusion can be drawn as to the relationship of the crystal structures of the two mixed substances. This must be all the more insisted upon, since not infrequently two substances are described as isomorphous merely on the ground of the behaviour of fused mixtures of them. This is the case, for example, as regards several substances examined by Bruni, their crystallographical relations being quite unknown.

The difficulties in the way of further progress in this department are increased by the fact that apparently homogeneous mixed crystals of continuously varying composition are obtainable with substances whose chemical nature is totally different, *i.e.*, the crystals of one substance are

capable of taking up another substance (not isomorphous with it) in variable proportions, though as a rule only to a limited extent, in a uniformly dilute condition. Here belong the numerous colorations of natural crystals (such as amethyst), the absorption of colouring matters by salts in the process of crystallisation, which thereby assume the optical properties of idiochromatic substances (*e.g.*, strontium nitrate with Turkey-red), the mixture of ammonium chloride with variously coloured metallic chlorides, (ferric chloride, etc.); such cases have been designated "anomalous mixed crystals," and, according to Johnsen, are to be looked upon, from the standpoint of the phase rule, as mechanical mixtures and not as "solid solutions."<sup>1</sup>

To the truly isomorphous mixtures, on the other hand, must be reckoned those cases in which two substances which, possessing a closely agreeing crystal structure but no completely analogous chemical constitution, form a continuous series of homogeneous mixed crystals—the triclinic feldspars, for example. The predilection towards certain definite mixture ratios in the series named is probably connected with the fact that apparently a regular distribution of the two kinds of atomic groups provides a particularly stable equilibrium of the crystal structure, since it occurs also with isomorphous substances of completely analogous chemical constitution.<sup>2</sup> The phenomenon would then find its analogue in the case of polysymmetric substances in the formation, at certain temperatures, of sub-microscopic lamellæ alternating so regularly that the simple form of higher symmetry

<sup>1</sup> This author has given, in the *N. Jahrb. f. Min.* 1903, 2, 93 *et seq.*, an excellent review of the observations regarding this phenomenon.

<sup>2</sup> Other facts also support the view that a greater stability of crystal structure exists in isomorphous mixtures when the constituents are present in simple molecular proportions; for example, the minimal vapour tension of such mixtures in the case of alums and of vitriols, as observed by Hollmann (*Zeits. f. phys. Chem.* 1901, 37, 193 *et seq.*; *Centralbl. f. Min.* 1904, 513; *Journ. C. S.* 80, ii. 436).



results ; this likewise points to the greater stability of such structures.

### *Polymorphous Transformations of Isomorphous Mixtures*

As the melting point of a crystallised substance is altered by an isomorphous admixture, such is also the case as regards the temperature of transformation into a polymorphous modification. Bellati and Lussena found that the transition temperature of potassium nitrate is lowered by addition of rubidium nitrate or thallous nitrate, and in the latter case the depression is, for small additions, proportional to the amount added ; Rothmund observed the same regularity in the depression of the transition temperature of carbon tetrabromide by small admixtures of tetrachloride. A general theory of the phenomena attending the transformation has been given by Roozeboom,<sup>1</sup> based on the phase rule. One of the cases so deduced was proved by Reinders in a comprehensive investigation which he made regarding mercuric bromide and iodide. By crystallisation after fusion, these yield a continuous series of isomorphous mixtures of the yellow (rhombic) modification. The transition point of rhombic mercuric iodide into the tetragonal form lies at  $127^{\circ}$  ; it is lowered by admixture of mercuric bromide, and this effect is represented by two curves (Fig. 6), between which there lies a transition interval, so that on one side of the one curve only  $\alpha$  crystals (the red tetragonal modification) can exist, while on the other side of the second curve only  $\beta$  crystals can exist. The fall of the curve is so steep that the corresponding transition point for the pure bromide must be very low ; as a matter of fact, mixtures rich in bromide remain permanently yellow even at very low temperatures.

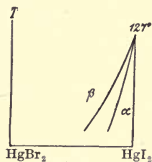


FIG. 6.

The last-mentioned facts contribute considerably towards

<sup>1</sup> *Zeits. f. phys. Chem.* 1899, 30, 413 ; *Journ. C. S.* 78, ii. 132.

an explanation of the relationships existing in the group  $\text{HgCl}_2\text{—HgBr}_2\text{—HgI}_2$ . Here we have to do with three modifications: I, the tetragonal form of the red iodide; II, the rhombic one of the bromide; and III, that of the chloride, which is likewise rhombic but is not isomorphous with the preceding one. According to observations by Lutschitzky, made in the author's laboratory, the bromide appears in form III. in isomorphous mixtures with the chloride, but in form I. in mixtures with the iodide when the crystals are rich in iodide; hence the isotrimorphism of the group is proved.

### *The Crystalline Forms of Isomorphous Mixtures*

As would be expected from the agreement in the symmetry of two truly isomorphous substances, mixtures of such substances also exhibit the same symmetry; hence it follows directly that two isomorphous cubic substances yield mixed crystals which geometrically are identical with those of the pure substances. As regards the faces which occur, these are, for isomorphous substances under the same conditions of crystallisation, generally the same, and likewise therefore for the mixtures. Should, however, the individual substances exhibit a difference in the extent to which they affect one or another form, and, consequently, a constant difference in the habits of their crystals (which, as a rule, appears to be more frequent with substances crystallising non-cubically), then the mixed crystals in many cases are of an intermediate habit. The mixed crystals of many isomorphous substances (*e.g.*, the hydrated sulphates of the green-vitriol type) as a rule form very simple combinations, whilst the crystals of the pure salts are often richer in faces; in other cases the crystals of isomorphous mixtures exhibit a great profusion of faces (*e.g.*, those of epidote and other minerals). In these latter cases we have to deal with crystals which, in addition, are very well formed, whilst in many cases the mixed crystals exhibit a less perfect development.

This latter circumstance gives rise to a special difficulty

in the investigation of the differences exhibited by the angles of non-cubic mixed crystals, relatively to the composition of the latter. The first attempt to investigate the manner in which the crystallographical dimensions of isomorphous mixtures depend on the proportions of the constituents in the mixture, was made by Groth, who employed for the purpose the perchlorates and permanganates of the univalent metals. The result was to show that the axial ratios of mixtures of potassium perchlorate and potassium permanganate do not lie between those of the pure salts; the same was proved for some other rhombic substances, and it was therefore concluded that the influence of the isomorphous admixture was different along the three non-equivalent axes, and was not proportional to their relative lengths. On the other hand, Dufet, on mixtures of Epsom salt and zinc vitriol, found the variations of the prism angle to be approximately proportional to the ratios in which the two salts were present. The difference for the pure salts amounts, it is true, only to  $0^{\circ} 37'$ , whilst all the other angles of the two sulphates differ still less from one another, so that no safe conclusions can be drawn from the measurements of the mixed crystals.

Apart altogether from the fact that in the first of the above-mentioned cases the mixed crystals examined showed somewhat considerable variations amongst themselves, and hence were not in all instances sufficiently homogeneous, the same objection arises against the comparison of the axial ratios here made as does against all comparisons which are not based upon the topic parameters (see page 38).

Those views regarding the crystal structure of isomorphous mixtures, which have already been propounded as fundamental (compare page 89), would lead us to expect that for the topic parameters of such mixtures there should exist the same dependence on composition which was found by Retgers to hold for the density. If, as in that case, we imagine the two components of a mixed crystal to be

present in uniform distribution, each retaining its own specific volume, then representing the topic parameters of the first substance by  $\chi_1$ ,  $\psi_1$ ,  $\omega_1$ , and those of the second substance by  $\chi_2$ ,  $\psi_2$ ,  $\omega_2$ , the parameters of an isomorphous mixture containing  $a_2$  per cent. by volume of the second substance would be given by the equations :

$$\chi = \chi_1 + a_2(\chi_2 - \chi_1)/100$$

$$\psi = \psi_1 + a_2(\psi_2 - \psi_1)/100$$

$$\omega = \omega_1 + a_2(\omega_2 - \omega_1)/100.$$

In order to test this regularity it would be necessary to select two substances which exhibit the greatest possible differences in their corresponding topic parameters, and of which, in addition, mixtures are easily obtainable in homogeneous and accurately measurable crystals varying widely in composition.

### *Optical Properties of Isomorphous Mixtures*

Since the molecular optical refraction of a chemical compound is composed of the values for the equivalent refractions of the individual elements of which the compound is composed,<sup>1</sup> the refractive indices of two isomorphous substances are always different. As regards mixtures of the two it is therefore to be expected, from what has already been considered, that they should possess refractive indices calculable from those of their components by a formula analogous to those assumed above for the topic parameters. This is confirmed by the observations so far made regarding the optical properties of isomorphous mixtures.

For the simplest case, that of singly refracting crystals, there exists the investigation of a mixture series of potassium alum and thallium alum by Fock, from whose results (as recalculated by Dufet) it appears that the refractive index changes proportionally with the composition of the mixture. According to Soret, the same holds for mixtures of potassium alum and ammonium alum.

As regards optically uniaxial crystals, mixtures of strontium

<sup>1</sup> See more particularly Pope, *Journ. C. S.* 1896, **69**, 1530; *Zeits. f. Kryst.* **28**, 113.

dithionate,  $\text{SrS}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ , and lead dithionate,  $\text{PbS}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ , exhibit, according to Fock's measurements, a proportionality between composition and the two principal indices of refraction (and also the rotatory power, according to Bodländer).

Finally, as regards optically biaxial crystals, rhombic substances have been investigated, especially by Dufet, who first showed the linear dependence of the three principal refractive indices on the composition in the case of isomorphous mixtures of magnesium sulphate with nickel sulphate and with zinc sulphate. This dependence is also shown very exactly by Lavenir's measurements on the two Rochelle salts. Since small differences in the refractive indices produce relatively large differences in the angles of the optic axes, this regularity can be tested more accurately by measurement of the axial angles of isomorphous mixtures; for from the known refractive indices of the two isomorphous substances the (theoretical) values for any mixture can be calculated, and from these theoretical refractive indices the appropriate axial angle can be deduced. The comparison of this value with the axial angle as determined directly on the mixed crystal, which was undertaken by Dufet for the sulphates already mentioned, as a matter of fact showed a very good agreement; so that it is possible, from the axial angle of a mixture, to decide as to the composition of the latter. Similar results were obtained by Mallard in the case of the sulphates and chromates of potassium and ammonium, which are likewise rhombic. With the latter, as with Rochelle salt, the case arises of the optic axes of two isomorphous substances lying in two different pinacoids. In the mixture series there is therefore, necessarily, first a gradual diminution of the axial angle, until, for a definite colour, and with a definite composition of the mixture, the two axes fall together, to be followed by a reappearance of the biaxial character with gradual increase of the axial angle in the new axial plane perpendicular to the first.

With monoclinic and triclinic crystals, in addition to the difference in the refractive indices, there arises the difference in the position of the principal vibration directions for two isomorphous substances, and this also may be considerable. Very complete investigations of such cases exist only as regards the mixtures of the feldspars, for which it has been found that there is a change in the orientation of the vibration directions which is proportional to the composition of the mixture.

In all the above-mentioned isomorphous mixtures we

are dealing with optically normal crystals. There also exist observations, however, which indicate the occurrence of optical anomalies resulting from isomorphous mixture. Thus, Klocke and Brauns observed that crystals of alum, which contained small quantities of an isomorphous compound, exhibited anomalous double refraction, whilst perfectly pure crystals possessed normal single refraction. Whereas the optical anomalies in this case probably depend on the existence of compression or extension stresses due to an incomplete equilibrium of the heterogeneous crystal structure, in other cases these anomalies may quite well be only apparent, and induced by polysynthetic twin structure.



## MOLECULAR COMPOUNDS

IN the preceding section (page 98), it was mentioned that isomorphous mixtures in simple stoichiometric proportions appear in certain cases to possess greater stability than do those in other proportions. Now, the view regarding crystal structure which has been here adopted, shows at once that the formation of a crystal from two different kinds of chemical molecules, even though these differ very slightly from each other, will give a particularly stable structure when the molecules take part in this formation in regularly alternating manner; since such a substance has as much right to the name of "molecular compound" as to that of "isomorphous mixture," it is evident that that view does not permit of any sharp boundary between the two ideas. It is also to be expected that the predilection for definite simple stoichiometric proportions will become more evident the greater the difference between the two constituents replacing one another in the components of the mixture.

An example of two substances which, in the narrowest sense of the term, are isomorphous, and yet exhibit peculiar points of greater stability in the series of mixtures which they form, is provided by the two sulphates of magnesium and zinc, investigated by Hollmann (see note, page 98).

As regards isomorphism, the two metals magnesium and calcium exhibit greater differences than magnesium and zinc do, and here the predilection for simple stoichiometric proportions appears much more strongly. Calcite,  $\text{CaCO}_3$ , and magnesite,  $\text{MgCO}_3$ , must, from their physical properties (crystalline form, cleavage,

etc.), still be described as isomorphous, and there undoubtedly occur mixtures of the two in varying proportions, though in these, as a rule, the one or the other salt preponderates greatly; in nature, however, it is mostly the double salt, dolomite,  $\text{CaCO}_3, \text{MgCO}_3$ , which has been formed, and that even in presence of excess of calcium carbonate. This double salt, whilst as regards the values of its angles, cohesion, etc., it occupies a position between its two components, nevertheless differs from them by possessing lower symmetry, corresponding to the less symmetrical crystal structure which results when this is considered as built up of alternate molecules of the two components. A maximum of stability in such a structure, as compared with those in which the atoms of calcium and of magnesium are present in different proportions, should also betray itself in determinations of the solubility—made, for example, by the method employed by Foote (see note, page 23)—by the occurrence of a minimum at this point in the series; that such is the case appears highly probable from the behaviour of dolomite towards acids, as observed by Haushofer and others. Precisely similar relationships are observed regarding the mixtures of the metasilicates,  $\text{CaSiO}_3$  and  $\text{MgSiO}_3$ , which, in the ratio 1 : 1, constitute the mineral diopside.

As appears from the considerations just adduced, there are transition stages between isomorphous mixtures and molecular compounds, and it is still less possible to draw a sharp boundary between molecular compounds and the "atomic" compounds. As is generally known, the designation **molecular compounds** has been applied to combinations of two or more compounds in each of which, according to the prevailing theory of valency, the affinities of the atoms are already fully satisfied, with formation of crystallised substances; the term is, however, merely a mode of expressing the fact that we are not in a position to explain the constitution of these substances. But, once the chemical nature of a number of these substances (the chloroplatinates, for example) had been shown to be that of salts of a complex acid, the frequently suggested probability of all such cases being true atomic compounds has steadily come to be more and more recognised. To Werner more especially is due the credit for having, on the basis of

geometrical representations (which are, it is true, purely theoretical, and stand in no relation to the crystal structures of the respective substances), shown the great probability of the direct union of the atoms which, on the earlier hypothesis, were looked upon as belonging to different molecules. The view regarding crystal structure which has been here adopted leads to exactly the same conclusion, when it is applied systematically to all crystallised substances—when, for example, the crystal structure of the double salt formed by one molecule of zinc chloride with two molecules of potassium chloride, corresponding to the formula  $K_2ZnCl_4$ , is conceived as consisting of three interpenetrating regular point-systems, of which the first contains twice, and the third, four times, as many atoms as the second. The manner in which such a crystal structure breaks up on dissolution must evidently depend on the nature of the atoms (*i.e.*, on the nature of their mutual union), on the solvent, the concentration of the solution, the temperature, etc., so that widely different kinds of disintegration are to be expected on the dissolution of substances of this kind, and such is indeed found to be the case. In like manner, also, would be explained the circumstance, so frequently observed with just these so-called molecular compounds, that the symmetry of the crystal structure stands in close relation to the number of similar atoms in the chemical molecule (see note, page 15).

A particularly interesting example of the substances under consideration is provided by the compounds containing so-called **water of crystallisation**, which, however, as is well known, cannot be separated from those containing so-called **water of constitution**. If these also, in the crystallised state, are considered as atomic compounds (which Werner has already done by the assumption of the replaceability of chlorine by water molecules), *i.e.*, if the oxygen and hydrogen atoms of the water are looked upon as constituents of the crystal structure just as much as the other atoms are, then all those difficulties disappear,

which hitherto the differentiation into water of crystallisation and of constitution has caused; it then becomes explicable why, in general, demolition of the crystal structure ensues on loss of water by efflorescence, and also why, in certain cases, some of the water molecules which result on efflorescence are liberated only at definite higher temperatures, as is the case, for example, with the vitriols. In the same way also an immediate explanation is supplied regarding the simple relation frequently observed between the number of water molecules and the number of similar atoms in the salt molecule, and, consequently, between it and the symmetry of the crystal structure.

The whole of the preceding considerations naturally apply likewise to the compounds containing so-called **benzene, alcohol, acetone, etc., of crystallisation.**

In the theory of crystal structure here adopted, the possibility is nevertheless not excluded that the atoms of the anhydrous compound, especially when this is of high molecular weight, should form closer atomic groupings, between which the atomic groups of the water occupy positions in such a way that, even after their removal by elevation of the temperature, the regular structure persists, though necessarily with altered physical properties. In that case these water groups must necessarily be endowed with an exceptional mobility. Behaviour of this kind is, as a matter of fact, exhibited by the zeolites, according to the researches of Mallard, G. Friedel, and others; the proportion of water in these compounds varies with the pressure of aqueous vapour in the surrounding atmosphere, and, once removed, the water is reabsorbed when the crystal is brought into moist air; or it may be replaced by hydrogen, hydrogen sulphide, ammonia, carbonic anhydride, or alcohol. A similar behaviour was also observed by Tammann in the case of the hydrates of magnesium platino-cyanide.

In the crystal structure of those zeolites which in composition correspond to hydrates of a felspar silicate, there is

found, in agreement with the considerations brought forward above, an unmistakable analogy with the crystal structure of the felspars. It is also possible that the relationships which Jaeger<sup>1</sup> found to exist between silver nitrate and its compounds with succino-nitrile, may be comparable with the above. An influence on the crystal structure by the predominating constituent of complex compounds is also shown in the case of the native basic thiarсенites and thiantimonites of silver (stephanite, polybasite, etc.) whose crystal forms show close affinity with those of the isomorphous sulphides of silver and copper,  $\text{Ag}_2\text{S}$  and  $\text{Cu}_2\text{S}$ .

In general, however, the relationships of the crystal structures of the so-called molecular compounds to those of their components have not yet been established, and require thorough systematic investigation.

### Racemic and Optically Active Compounds

The crystallised racemic substances are molecular compounds which by solution or fusion become converted into a mixture of two optical antipodes, and this mixture is optically inactive, since it contains the two components in exactly equal proportions. In order to obtain a representation of the crystal structure of the racemic compounds, it is necessary, first of all, to consider that of optically active substances, and this we shall now proceed to do.

To those organic substances whose solutions possess the power of rotating the plane of polarisation of light must be ascribed, as le Bel and van't Hoff have shown, a chemical structure such that the molecules of the dextro (*d.*) and of the lævo (*l.*) substance are mirror images the one of the other, but are not superposably alike. Two solid structures which stand in this relation are said to be **enantiomorph**. The important connection which exists between the enantiomorph nature of the optically active substances and their crystalline form was first recognised by Pasteur ;

<sup>1</sup> *Zeits. f. Kryst.* 1903, 37, 341.

it can be expressed as follows: *the two optical antipodes of an optically active compound possess enantiomorph crystal structure.* They therefore exhibit identity of scalar properties (density, melting point, solubility, heat of dissolution and of combustion, etc.), as also of optical and other ellipsoidal properties, of cleavage, and of elasticity. Finally, the crystal angles of the two substances are the same, while their crystal forms stand to one another in enantiomorphous relationship. As a consequence of the last-mentioned circumstance, the crystal forms of an optically active substance always belong to one of those symmetry classes in which planes of symmetry—simple or compound—are entirely wanting, *i.e.*, in the case of triclinic crystals, to the asymmetric class; in monoclinic, to the sphenoidal class; in rhombic, to the bisphenoidal class; in trigonal, tetragonal, and hexagonal, to either the pyramidal or the trapezohedral class of the respective systems; in cubic crystals, finally, to the tetrahedral-pentagonal-dodecahedral or the pentagonal-icositetrahedral class.<sup>1</sup>

Since, amongst the simple crystal forms of the classes possessing enantiomorph symmetry, those with the simplest symbols (*i.e.*, the commonest forms) are generally such that the right and left forms, when considered from the purely geometrical standpoint, cannot be distinguished from one another, it frequently happens that the crystal forms of two optical antipodes exhibit apparent identity; namely, when the only forms which occur are of the above-mentioned kind (for example, combinations of the prismatic forms of the rhombic system), or when non-equivalent faces, such as the parallel ones at the opposite poles of the symmetry axis of a monoclinic sphenoidal crystal, appear to be similar and similarly developed. In such cases the enantiomorphism can be recognised only by the investigation of those properties which alone are suitable for the conclusive determination of the symmetry of a crystal, *i.e.*, by noting the

<sup>1</sup> For examples of these classes, see the author's *Physikalische Krystallographie*.



occurrence of pyro-electric polarity, enantiomorphous erosion figures, or unequal development of the non-equivalent faces under certain conditions of crystal formation.

According to the theory of crystal structure here adopted, the enantiomorphism of the crystal structures of two optical antipodes appears as a direct consequence of the enantiomorphism of their chemical molecules; for, according to it, the interpenetration of the regular point-systems, each consisting of different atoms, is such that the relative position of the atoms is the same as in the chemical molecule. Hence the crystal structure whose demolition on dissolution yields only lævo-rotatory molecules must be the mirror image of that structure which, on dissolution, yields only dextro-rotatory molecules. Here, therefore, the manner of interpenetration of the point-systems determines the absence of a plane of symmetry for the whole structure, and, therefore, the existence of two mirror-image structures.

As Sohncke has shown, a regular point-system may, however, in itself be so constituted that two enantiomorphous forms of it are possible—when, namely, it possesses a right or a left spiral arrangement of the points; and, as is well known, the so-called **crystal rotation** (*i.e.*, the property which certain *crystals* possess of rotating the plane of polarisation of light) is explicable in this way. If, in an optically active crystal, the interpenetration of the point-systems is such that the atomic groups corresponding to them, into which the crystal structure is resolved on dissolution, are incapable of enantiomorphism, then the solution exhibits no optical activity. We have then to deal merely with crystal rotation, which is purely and simply a consequence of the nature of the point-systems constituting the crystal structure, and whose extended treatment belongs to the domain of physical crystallography.

In the case of the crystals of substances which are optically active in solution, however, we have to deal, on the one hand, with the so-called **molecular rotation**, the

rotation caused by the molecules (*i.e.*, by the mode of interpenetration of the point-systems in the crystal), and, on the other hand, with the crystal rotation, which is combined with the other when, to the enantiomorphism of the mode of interpenetration of the point-systems, there is added an enantiomorphism inherent in these themselves. As a matter of fact, this appears generally to be the case; and when the molecular rotation, as obtained either by direct measurement on the amorphous (fused) substance itself, or by calculation from the rotatory power of the solution, is compared with the rotation observed on the crystals, it is found that the latter effect is derived principally from the crystal rotation.

According to the investigations of H. Traube,<sup>1</sup> the rotatory power of **matico camphor**,  $C_{12}H_{20}O$ , referred to unit density, is, for 1 mm., in the amorphous state,  $-0.29^\circ$ ; and in the crystallised state,  $-2.07$ . The corresponding values for **cinchonine antimonyl d-tartrate**,  $2(C_{19}H_{22}N_2O, SbC_4H_4O_7), 5H_2O$ , are:  $+4.14^\circ$  and  $+9.79^\circ$ ; for **zinc hydrogen malate**,  $Zn(HC_4H_4O_5)_2, 2H_2O$ , the values are:  $-0.55^\circ$  and  $-3.02^\circ$ . In the case of **rubidium d-tartrate** the crystals are lævo-rotatory,  $\alpha_D = -10.24^\circ$ , while the molecular rotation of the amorphous substance is  $+0.69^\circ$ . Since the latter possesses the opposite sign, the actual crystal rotation in this case amounts to  $-10.93^\circ$ . Similarly, the rotatory power of **sucrose**,  $C_{12}H_{22}O_{11}$ , is, according to Pocklington,<sup>2</sup> much stronger in the crystallised state than in the amorphous state. On the other hand, the rotatory power both of **patchouli camphor**,  $C_{15}H_{26}O$ , and of **laurel camphor**,  $C_{10}H_{16}O$ , has been found to have about the same value as the molecular rotation, and therefore appears to result essentially from the latter.

In accordance with the view developed for optically active substances, the crystal structure of a *racemic* carbon compound is to be viewed thus: Since the "asymmetric carbon atoms," which are surrounded by the other atoms in an enantiomorphous arrangement, must consequently possess different orientations, they necessarily form an

<sup>1</sup> *Zeits. f. Kryst.* 1894, 22, 50; 1899, 31, 624.

<sup>2</sup> *Phil. Mag.* 1901 [6], 2, 361; *Zeits. f. Kryst.* 37, 292.

even number of space lattices, two at least. Each of the remaining point-systems composed of similar atoms must also be so constituted that the arrangement of the one half of the atoms represents the mirror image of the arrangement of the other half, and so the possibility is provided that the complete structure of the crystal should possess planes of symmetry. The system of asymmetric carbon atoms in such an arrangement would then bear the same relation to that of one of the two optical antipodes as do the point-systems, composed of carbon atoms, in the crystal structure of two substances which stand in polymeric relationship to one another; and since, in two substances of the latter kind, the conditions of equilibrium are totally different, an essential difference of crystal structure is to be expected between racemic substances and their optically active components, notwithstanding certain points of relationship between them.

The enantiomorph crystals of optically active substances often unite to form twins, so that yet another kind of combination of the two optical antipodes, in equal quantities, is conceivable—that, namely, of a structure consisting of equally thin sub-microscopic twin-lamellæ, alternately dextro and lævo. Such a crystal structure would represent the complete analogue of the more symmetric form of a polysymmetric substance (page 6), and must necessarily possess the same density, specific heat, melting point, etc., as the two optical antipodes; and its crystal form would differ from the forms of the latter only by the symmetry on the twinning plane, and by the equalisation of those angles which are different for the two positions, brought about by the twin structure. This case probably occurs with those substances which Pope<sup>1</sup> called **pseudo-racemic**, and has explained by the assumption of a lamellar twin structure. According to Kipping and Pope, the circumstance that the

<sup>1</sup> See Kipping and Pope, *Journ. Chem. Soc.*, 1897, 71, 989, 1899, 75, 1121; *Zeits. f. Kryst.* 1899, 30, 461.

melting point of such a substance does not always coincide with that of the optically active components depends on the fact that a substance which is pseudo-racemic at ordinary temperatures, may, on heating, become transformed into a racemic one, and naturally it then possesses the melting point of the racemic substance. Conversely, a substance which is racemic at ordinary temperatures may melt as such, or it may first decompose into a mixture of the two active constituents; in the former case the melting point is different from that of the two active substances, in the latter case it is the same. This is simply a consequence of the general dependence on temperature, to which the crystal structure of substances in general is subject.

In the following paragraphs these relationships will be explained more fully by means of actual examples, beginning with substances which are undoubtedly racemic.

**Racemic acid**, (*r*-) $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , crystallises in the triclinic pinacoidal class, and, according to its angles and cleavage, possesses a crystal structure which is quite different from that of the two active tartaric acids, which are monoclinic sphenoidal, a difference pointed out by A. Scacchi.<sup>1</sup> The densities were determined by Liebisch,<sup>2</sup> who found: for racemic acid,  $D = 1.788$ , for the two tartaric acids,  $D = 1.759$ . As regards the salts of the acids, it has been stated that potassium hydrogen racemate, (*r*-) $\text{KHC}_4\text{H}_4\text{O}_6$ , and potassium hydrogen tartrate, (*d*-) $\text{KHC}_4\text{H}_4\text{O}_6$ , have approximately the same axial ratios. Apart from the facts that their symmetry is different, and that in the case of the former salt there exist contradictions, still not cleared up, between the determinations made by Scacchi and those by Wyruboff, the two compounds differ as regards their cleavage, and have certainly a totally different crystal structure. For the density of the racemate, Wyruboff gives a number which agrees exactly with that of Buignet for the tartrate. It is evident that the racemates and the tartrates require further systematic and comparative investigation.

**Aspartic acid**,  $\text{H}_2\text{C}_4\text{H}_3\text{NH}_2\text{O}_4$ ; the racemic compound, which is monoclinic prismatic, and the active ones, which are rhombic

<sup>1</sup> D. acido parataratarico anidro, *Atti. R. Accad.*, Naples, 1869.

<sup>2</sup> *Ann. d. Chem.*, 1895, 286, 140.

bisphenoidal, exhibit no crystallographical resemblances. (Cleavage and density apparently have not been determined.)

**Malic acid**,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_5$ , is crystallographically still insufficiently investigated. The acid ammonium salt of the racemic acid and that of the active acid crystallise quite differently; the density is known in the case of the latter only.

**Benzoyltetrahydroquinoline**,  $\text{C}_{10}\text{H}_{12}\text{NCOC}_6\text{H}_5$ . The racemic substance has the density 1.2375, and is monoclinic prismatic; the active one has the density 1.2114, and is monoclinic sphenoidal. The crystal forms of the two exhibit no similarity.<sup>1</sup>

**Carvoxime**,  $\text{C}_{10}\text{H}_4\text{NOH}$ . Both the racemic and the active substances crystallise monoclinic, and have very similar axial ratios, while the axial angles  $\beta$  show a greater amount of discrepancy. The density of the former is 1.126; that of the latter, 1.108; the solubility curves of the two are also different.

**Limouene tetrabromide**,  $\text{C}_{10}\text{H}_{12}\text{Br}_4$ . In the form of the racemic compound this substance, formerly called dipentene tetrabromide, has the melting point  $125^\circ$ , and density 2.225, and crystallises rhombic bipyramidal. The active substance, likewise rhombic, has a very similar habit, and axial ratios which differ only slightly from those of the former; the subsidiary forms, as also the symmetry, are of course different. Its melting point is  $104^\circ$ , and its density 2.134. An ethereal solution of equal quantities of the active and inactive substances yields no mixed crystals, but separate crystals of melting points  $125^\circ$  and  $104^\circ$  respectively (Wallach).

**Benzylidene camphor**,  $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CH} \cdot \text{C}_6\text{H}_5$ . The racemic substance has the melting point  $73^\circ$ , and forms monoclinic prismatic crystals, totally different from the rhombic bisphenoidal form of the active components; these have the melting point  $98^\circ$ , and the density, within the limits of experimental error, agrees with that of the racemic substance.<sup>2</sup>

As shown by these and other examples, racemic substances in general possess a crystal structure different from that of the optically active components, as is the case with isomeric substances generally. As a rule, the racemic substance possesses the higher density, lower solubility, and higher melting point. When the melting point coincides

<sup>1</sup> Pope and Peachey, *Journ. C.S.* 1899, **75**, 1066 *et seq.*; *Zeit. f. Kryst.* **34**, 612 *et seq.*

<sup>2</sup> Minguin, *Zeits. f. Kryst.* 1904, **39**, 317.

with that of the active substance, it is to be assumed that the racemic compound, before melting, undergoes transformation into a mixture of the two optical antipodes.

The following substances, it seems probable, belong to the class of pseudo-racemic compounds, in which the never-failing resemblance between their crystal forms and those of their optically active components is, as stated on page 113, best explained by the assumption of a sub-microscopic lamellar structure composed of equal proportions of the two components :

**Calcium hydrogen malate**,  $\text{Ca}(\text{HC}_4\text{H}_4\text{O}_6)_2 \cdot 6\text{H}_2\text{O}$ . When prepared from the racemic acid, this salt, according to Pasteur, has the same form and cleavage as the salt prepared from the active acid, only the hemihedral faces are wanting. Further data are not available.

**Sobrerol**,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ . When crystallised from an alcoholic solution of a mixture of equal parts of the two active substances, this compound is rhombic, and its form, as regards the axial ratios, optical properties, habit, and cleavage, is almost identical with that of the two active components; these form monoclinic sphenoidal crystals, and exhibit twinning on the plane which is to be assumed as the plane of polysynthetic structure for the pseudo-racemic rhombic crystals.<sup>1</sup> The densities of the rhombic and of the monoclinic crystals likewise coincide within the limits of experimental error, but the melting-points are different; in order to explain this difference, it must be assumed that the rhombic crystals, on heating, become transformed into a truly racemic compound, whose melting point, naturally, is different from that of the monoclinic crystals.

**w-Bromocamphoric anhydride**,  $\text{C}_{10}\text{H}_{13}\text{BrO}_3$ , has, both in the inactive and in the optically active states, the same crystalline form and the same melting point.<sup>2</sup>

**Bromobenzylidene camphor**,  $\text{C}_{17}\text{H}_{19}\text{BrO}$ , when crystallised from

<sup>1</sup> Armstrong and Pope, *Journ. C. S.* 1891, 59, 317; Miers and Pope, *Zeits. f. Kryst.* 1892, 20, 321 *et seq.*

<sup>2</sup> Kipping and Pope, *Journ. C. S.* 1897, 71, 1000; *Zeits. f. Kryst.* 30, 470. The dipentene hydrochloride nitrolanilide, mentioned at the same place, does not belong to this class, as the two substances have since been proved to be identical, and racemic.



equal quantities of the two optical antipodes, exhibits the same forms as these do, but lacks the pyramidal faces characteristic of the sphenoidal hemihedrism of the active substances; it has the same density. The difference of melting point is to be referred to a transformation, on heating (but previous to fusion), of the pseudo-racemic substance into a truly racemic one.

**Camphorsulphonic chloride**,  $C_{10}H_{15}O.SO_2Cl$ , crystallises from a mixture of the two antipodes in rhombic bipyramidal crystals, which, though they cannot be completely measured, have axial ratios and optical properties similar to those of the two components, which form rhombic bisphenoids. The lower melting point of the bipyramidal crystals is undoubtedly due to a transformation into a racemic substance.<sup>1</sup>

**trans-Camphotricarboxylic anhydride**,  $C_{10}H_{12}O_5$ , exhibits, both in the active and in the inactive states, monoclinic crystals with similar habit, identical cleavage, and angles as nearly alike as those of isomorphous substances; the crystals of the inactive substance, however, are less completely developed, and exhibit quite distinctly irregularities of formation. Density and melting point are exactly the same for both.<sup>2</sup> With regard to this example (and also to another mentioned in the paper quoted), it must be remarked, however, that the crystalline form of the inactive substance cannot well be derived from that of the active substances by twin formation.

As appears from the preceding examples, there is, as yet, no conclusive evidence to show that the so-called pseudo-racemic substances are built up by a regular sub-microscopic intergrowth of the two active components, though in many cases this seems highly probable. Since also, as shown on page 115, substances which are undoubtedly racemic may exhibit certain similarities between their crystalline forms and those of the active substances, it would require, in order to arrive at a definite conclusion, a very thorough investigation of all the crystallisation relationships of such substances, and, above all, an exact

<sup>1</sup> Kipping and Pope, *Journ. C. S.* 1893, 63, 554; 1897, 71, 996; *Zeits. f. Kryst.* 25, 225 et seq.; 30, 467.

<sup>2</sup> Kipping and Pope, *Journ. C. S.* 1897, 71, 986, 995; *Zeits. f. Kryst.* 1899, 30, 456, 466,

study of the transformation phenomena exhibited by them ; these may here be of totally different kinds—such, namely, as are caused by the existence of polymorphous modifications, and such as depend on the transformation of a mixture of the dextro and lævo substances into the racemic, and *vice versa*. The criteria which have been deduced from the phase rule by Roozeboom,<sup>1</sup> for distinguishing by solubility and melting point between racemic and pseudo-racemic compounds, on the one hand, and mechanical conglomerates of the optical antipodes, on the other, are of importance in this connection. (See also Adriani's paper on the solidification and transformation phenomena exhibited by optical antipodes.<sup>2</sup>)

As the number of well crystallised substances, concerning which we know with certainty that they stand mutually in the relation of racemic compound and its optically active components, is steadily increasing, especially by reason of the progress being made in the chemistry of the terpenes there is no lack of material for investigations, which, if carried out systematically on a large number of substances in the manner indicated above, would serve to elucidate finally the relationships between the crystal structures of the optical antipodes and that of their racemic and pseudo-racemic compounds.

<sup>1</sup> *Zeits. f. Phys. Chem.* 1899, **28**, 494 *et seq.* ; *Journ. C. S.* **76**, ii. 401.

<sup>2</sup> *Zeits. f. Phys. Chem.* 1900, **33**, 453 *et seq.* ; *Journ. C. S.* **78**, ii. 462.

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